

ความสัมพันธ์ระหว่างประวัติทางความร้อนกับสมบัติทางกายภาพของพอลิโอฟีนส์



นาย กิตติศักดิ์ ชัยเจริญ

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ภาควิชาวัสดุศาสตร์

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2546

ISBN 974-17-4505-2

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

RELATIONSHIPS BETWEEN THERMAL HISTORY AND PHYSICAL PROPERTIES OF POLYOLEFINS



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สถาบันวิทยบริการ

A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science in Applied Polymer Science and Textile Technology

Department of Materials Science

Faculty of Science

Chulalongkorn University

Academic Year 2003

ISBN 974-17-4505-2

Thesis Title Relationships between Thermal History and Physical Properties  
of Polyolefins  
By Mr.Kittisak Chaicharoen  
Field of Study Applied Polymer Science and Textile Technology  
Thesis Advisor Assistant Professor Pranut Potiyaraj, Ph.D.

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กิตติศักดิ์ ชัยเจริญ : ความสัมพันธ์ระหว่างประวัติทางความร้อนกับสมบัติทางกายภาพ  
ของพอลิโอเลฟินส์. (RELATIONSHIPS BETWEEN THERMAL HISTORY AND  
PHYSICAL PROPERTIES OF POLYOLEFINS) อ.ที่ปรึกษา : ผศ.ดร.ประณัฐ โพธิยะราช,  
96 หน้า. ISBN 974-17-4505-2.

งานวิจัยนี้มุ่งศึกษาถึงการเปลี่ยนแปลงโครงสร้างโมเลกุล สมบัติด้านแรงดึง และการ  
ขึ้นเหลืองของพอลิโอเลฟินส์ที่ผ่านการรีไซเคิลจำลองโดยการขึ้นรูปซ้ำเป็นจำนวน 10 รอบ พอลิ  
โอเลฟินส์ที่เลือกศึกษาได้แก่พอลิโพรพิลีน พอลิเอทิลีนชนิดความหนาแน่นสูง และพอลิเอทิลีนชนิด  
ความหนาแน่นต่ำ ทั้งเกรดอัดรีดและเกรดฉีด โดยนำพลาสติกที่ผ่านกระบวนการขึ้นรูปในแต่ละ  
รอบมาทดสอบหาดัชนีการไหล การดูดกลืนแสงอินฟราเรด ความทนแรงดึง การยืดตัว มอดุลัส  
และดัชนีความเหลือง จากผลการทดลองพบว่าพลาสติกทั้ง 3 ชนิด มีสมบัติที่เปลี่ยนไปจากเดิม  
โดยพอลิโพรพิลีนจะมีค่าดัชนีการไหลเพิ่มขึ้น เนื่องจากเกิดการขาดของสายโซ่โมเลกุลซึ่งได้รับ  
ความร้อนและความเค้นในระหว่างการขึ้นรูป เมื่อพิจารณาค่าดัชนีเมทิลซึ่งบ่งถึงการเปลี่ยนแปลง  
ของหมู่  $-CH_3$  เทียบกับหมู่  $-CH_2-$  พบว่ามีหมู่เมทิลมากขึ้นแสดงถึงความยาวของสายโซ่โมเลกุลซึ่ง  
สั้นลง ทำให้ค่าความทนแรงดึง การยืดตัว และมอดุลัสมีแนวโน้มต่ำลง ส่วนค่าดัชนีการไหลของพอลิ  
เอทิลีนจะมีค่าต่ำลง สันนิษฐานว่าปริมาณการเชื่อมขวางระหว่างสายโซ่มีมากกว่าปริมาณการ  
ขาดของสายโซ่ ทำให้น้ำหนักโมเลกุลเพิ่มขึ้น ผลดังกล่าวสอดคล้องกับดัชนีเมทิลซึ่งมีค่าลดลง  
ส่วนความทนแรงดึงและมอดุลัสมีค่าเพิ่มขึ้น ในขณะที่การยืดตัวออกมีค่าลดลง ในกรณีของพอลิ  
เอทิลีนชนิดความหนาแน่นสูงที่จำนวนรอบสูงๆ พบว่าเกิดการขาดของสายโซ่มากขึ้น จนทำให้ดัชนี  
การไหลมีค่าเพิ่มขึ้น และความทนแรงดึงและมอดุลัสมีค่าลดลง ในกระบวนการฉีดพลาสติกการ  
เปลี่ยนแปลงเหล่านี้จะเกิดขึ้นในอัตราที่สูงกว่าในกระบวนการอัดรีด เนื่องจากมีความเค้นใน  
ระหว่างกระบวนการมากกว่า นอกจากนี้ยังพบว่าทั้งพอลิโพรพิลีนและพอลิเอทิลีนจะเกิดการขึ้น  
เหลือง โดยเมื่อตรวจสอบดัชนีความเหลือง พบว่าพอลิเอทิลีนมีอัตราการขึ้นเหลืองสูงกว่าพอลิ  
โพรพิลีน สันนิษฐานว่าพอลิโพรพิลีนมีหมู่แทนที่ส่งผลให้เกิดหมู่โครโมฟอร์ได้ยาก

ภาควิชา วัสดุศาสตร์

ลายมือชื่อนิสิต.....

สาขาวิชา วิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ลายมือชื่ออาจารย์ที่ปรึกษา.....

ปีการศึกษา 2546



## ACKNOWLEDGEMENTS

The research presented in this thesis was carried out at Department of Materials Science, Faculty of Science, Chulalongkorn University. Numerous people are instrumental to the completion of this thesis and have offered me with valuable insights as the project progressed. Special thanks are due to my advisor (Assistant Professor Pranut Potiyaraj, Ph.D.) for helping the author to make this thesis and suggestion.

My sincere gratitude goes to Mr.Somkhid Thongsila for his kind assistance during laboratory work. I am grateful to Department of Production Engineering, King Mongkut's Institute of Technology North Bangkok for the permission to use the injection molding machine.

I am greatly indebted to the thesis committee, namely, Associate Professor Saowaroj Chuayjuljit, Associate Professor Paiparn Santisuk, Assistant Professor Duangdao Aht-Ong, Ph.D. and Assistant Professor Ratjana Sirisook for their valuable suggestions without which this thesis could not be produced in the present form.

I would like to thank all my friends and colleagues at Department of Materials Science for their interest, support, and valuable discussion during the course of my work.

My acknowledgement would not be completed without expressing my wholeheartedly thanks to my father, my mother and my sisters who constantly provide emotional support and take care of me in every aspects.

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## Chapter 1

### INTRODUCTION

The largest number of different polymeric materials possibly comes under the plastic classification. The word “plastics” comes from the Greek verb “to form” because they can be shaped and molded easily. There have been tremendous advance in plastic technology since the second half of the twentieth century because they are lightweight, low cost, energy saving, chemical resistant, thermal and electrical insulator, tough and durable.

Plastics are classified based on their heat response into two major groups: thermosets and thermoplastics. A thermoset is a polymer that solidifies or sets irreversibly when heated, but some thermoset did not solidify by heating. They are useful for their durability and strength, and are therefore used primarily in automobiles and construction applications. Other uses are adhesives, inks, and coatings. A thermoplastic is a polymer in which the molecules are held together by weak bonds, creating plastics that soften when exposed to heat and return to original condition at room temperature. Thermoplastics can easily be shaped and molded into products such as milk jugs, floor coverings, credit cards, and carpet fibers. Of the most common thermoplastic resins, polyolefins, especially polyethylene (PE) and polypropylene (PP), are popularly used as commodity plastics for variety of day life products.

Thermoplastic resins can be mixed with colorants and additives and are then processed in several ways, including extrusion, injection, blow, and rotational molding. All of these processes involve using heat and/or pressure to form plastic resin into useful products, such as containers or plastic film. In the extrusion process, plastic resins or pellets are fed into an extruder through a heated barrel where one or two screws turn continuously, mixing, blending, and melting the plastic to the end where the die is located. Depending on the shape of the die, a variety of objects are developed. Some common extruded products include drinking straws, molding strips, hose and tubing,

seamless gutters, window frames, and vinyl siding. A process similar to extrusion is the production of sheets and films. Plastic pellets are also used to produce injection molded products. The process is very similar to extrusion except the melted plastic is forced under pressure into a closed mold. After the mold is filled it is cooled, the two parts of the mold open, and the object drops out. Another molding process requires plastic pellets to be ground into a fine powder. The powdered plastic is easily melted and used for rotational molding. Rotational molding is used to make large toys and lawn mower catchers. This is becoming a more popular form of molding and is characterized by the object being hollow.

As plastics become so popular, many parts of the industrial world face serious problems of managing the generation and disposal of plastic wastes. Plastic recycling has emerged as a resolution to the problems since virtually all plastics can be recycled. The extent to which they are recycled depends upon both economic and logistic factors. In all of the processes used to convert plastic raw materials into end products there is an inevitable arising of some scrap material. This results from the start-up and shutdown periods of the processing machinery, from out of specification products and from quality control samples. Material of this type is termed industrial scrap. Almost all molding companies recycle their own plastics waste, or scrap, in house. The specialist plastics recycling industry also recycle material of this type, mostly skeletal waste from thermoforming and off-specification moldings. Some 250,000 -300,000 tones of plastics are dealt with in this way annually. Where the origin of the material is industrial scrap, the recovered end-product is generally referred to as 'reprocessed' to distinguish it from 'recycled' material which is derived from genuine post-consume products.

There is also some recycling of plastics products which have undergone a full service life and is then reclaimed for further use. Material of this type is called post-consumer material. It can arise from industrial, commercial and domestic sources. Recent years have seen a growth in post-consumer plastics recycling. Most of the plastics recycled are from the commercial and industrial sectors, with bottles being recovered from domestic sources. This pattern is because the main requirements for



effective recycling of post-use plastics are resource efficient reclamation of the post-use products, facilities to sort and compact the reclaimed products and end use applications for the recycled plastics materials. These conditions are more easily met from commercial post-use waste. In addition heavily contaminated waste requires special washing and drying facilities.

It is recognized that the recycling of industrial plastics are often more valuable than those of post-consume plastics. The recovery of post-consume plastics is complicated by a number of unique challenges, such as a much wider range of different and incompatible plastics; a less developed collection infrastructure; more varied end products; lower overall volumes of these materials, particularly on an individual grade basis; and a much wider range of attached foreign materials such as metal, rubber, foams, fabrics, etc.

During recycling process, plastics undergo processing under stress and heat, resulting in degradation of plastics. The degradation of plastics can be said to begin as soon as the polymer is synthesized, and is increased by residual stresses left by molding processes. This can be followed by exposure to light (especially UV), humidity, oxygen, heat, bacteria and stress. Plastics can also be contaminated by other materials, including other plastics. There are two main types of plastics degradation: physical and chemical, and both are closely inter-connected. Physical degradation can involve environmental stress cracking and plasticizer migration and loss. Chemical reactions include oxidation and hydrolysis.

In this work, polyethylene and polypropylene were repeatedly processed under different processing methods, i.e. extrusion and injection moldings. As affected by their thermal history, physical and mechanical properties of these reprocessed plastics, including melt flow indices, tensile strength and yellowness index, were investigated. Infrared spectroscopy was also used for studying chemical changes in the recycled plastics. The experimental results were subsequently interpreted so as to explain the degradation behavior of the polyolefins under different processing methods. This led to the correlations between thermal history and properties of polyolefins. These

relationships would be of interest to industry for reprocessing and recycling of polyolefins.



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## Chapter 2

### LITERATURE REVIEW

Plastics are organic polymeric materials consisting of giant organic molecules. Elastic materials can be formed into shapes by one of a variety of processes, such as extrusion, injection, casting or spinning. Modern plastics possess a number of extremely desirable characteristics; high strength to weight ratio, excellent thermal properties, electrical insulation, resistance to acids, alkalis and solvents, to name but a few. These polymers are made of a series of repeating units known as monomers. The structure and degree of polymerisation of a given polymer determine its characteristics. Linear polymers (a single linear chain of monomers) and branched polymers (linear with side chains) are thermoplastics that is they are soften when heated. Cross-linked polymers (two or more chains joined by side chains) are thermosetting that is they are harden when heated.

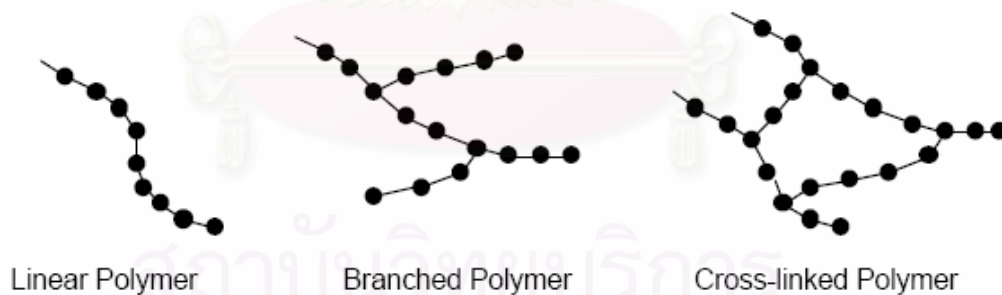


Figure 2.1 Polymer structures

Thermoplastics make up 80% of the plastics produced today. Examples of thermoplastics are:

- high density polyethylene (HDPE) used in piping, automotive fuel tanks, bottles and toys,
- low density polyethylene (LDPE) used in plastic bags, cling film and flexible containers,

- polyethylene terephthalate (PET) used in bottles, carpets and food packaging,
- polypropylene (PP) used in food containers, battery cases, bottle crates, automotive parts and fibers,
- polystyrene (PS) used in dairy product containers, tape cassettes, cups and plates,
- polyvinyl chloride (PVC) used in window frames, flooring, bottles, packaging film, cable insulation, credit cards and medical products.

There are hundreds of types of thermoplastic polymer, and new variations are regularly being developed. In developing countries the numbers of plastics in common use, however, tends to be much lower. Nowadays, the raw materials for plastics come mainly from petrochemicals, although originally plastics were derived from cellulose, the basic material of all plant life.

In 2002, the large-volume thermoplastic families of PE, PP, PVC, PS and PET represented 78 per cent of total plastics consumption in typical plastics applications as shown in Figure 2.2. (The Association of Plastics Manufacturers in Europe, 2003) Many of these demonstrated substantial growth, in particular PP with 11.4 per cent higher volumes, followed by LLDPE with 7.9 per cent increase, and HDPE 7.7 per cent. However, PVC demand was relatively flat, particularly between 2001 and 2002.

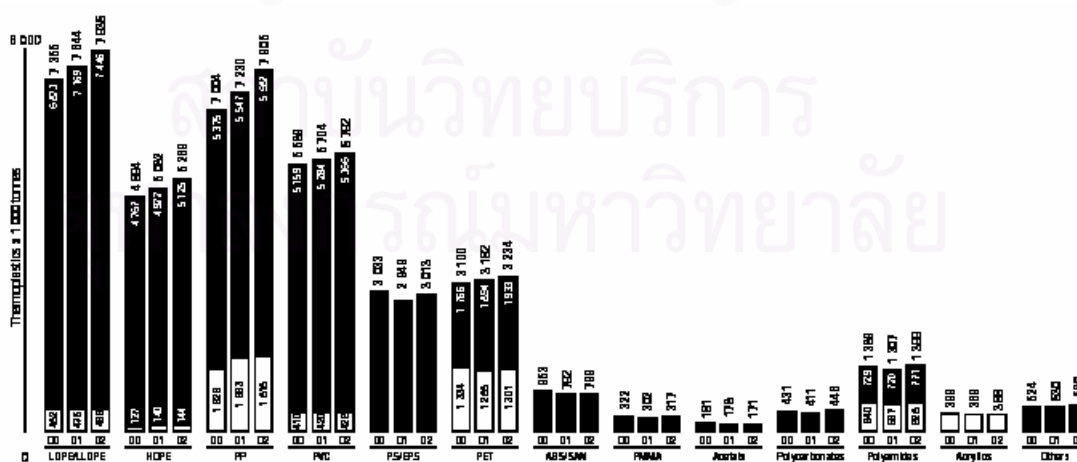


Figure 2.2 Consumption of plastics by type

## 2.1 Polyethylene (PE) (Brydson, 1972: 98-106 )

Emerging in the prewar period, Reginald Gibson and Eric Fawcett discovered another important plastic, polyethylene (PE), sometimes known as polythene, in 1933, at the British industrial giant Imperial Chemical Industries (ICI). This material evolved into two forms, low density polyethylene (LDPE) and high density polyethylene (HDPE). PE is cheap, flexible, durable and chemically resistant. LDPE is used to make films and packaging materials, while HDPE is used to containers, pipes and automotive fittings. While PE has low resistance to chemical attack, it was found later that a PE container could be made much more robust by exposing it to fluorine gas, which modified the surface layer of the container into the much tougher polyfluoroethylene.

### 2.1.1 Polymerization of Polyethylene

There are four quite distinct routes to the preparation of high polymers of ethylene, namely, high pressure process, Ziegler process, the Phillips process and the Standard Oil process. A brief explanation of each process is given below.

#### 2.1.1.1 *High Pressure polymerization*

Polyethylene is produced in this process under conditions of high pressure (1,000-3,000 atm) and at temperatures of 80 – 300°C. A free radical initiator such as benzoyl peroxide, azo-di-isobutyronitrile or oxygen is commonly used. The process must be operated by the reactants. Because of the higher heat of polymerization, care must be taken to prevent runaway reaction. This can be done by having a high cooling surface-volume ratio in the appropriate part of a continuous reactor and in addition by running water or a somewhat inert liquid such as benzene. The high pressure polymerization of ethylene has two particular characteristics, the high exothermic reaction and a critical dependence on the monomer concentration. The highly exothermic reaction has already been mentioned. It is particularly important to realize that at the elevated temperature employed, other reactions can occur leading to the formation of hydrogen, methane and graphite. Most ethenoid monomers will polymerize by free radical initiation over a wide range of monomer concentration. In the case of

ethylene, only low molecular weight polymer is formed at low pressure but high molecular weights are possible at high pressures. It would appear that growing ethylene polymer radical have a very limited life available for reaction with monomer. Unless they have reacted with in a given interval they undergo changes which terminate their growth. Since the rate of reaction of radical with monomer is much greater with higher monomer concentration (high pressure). It will be appreciated that the probability of obtaining high molecular weights is greater at high pressures than at low pressures. At high reaction temperatures (e.g. 200°C) much higher pressure are required to obtain a given concentration or density of monomer than at temperature of say 25°C and it might appear that better results would be obtained at lower reaction temperatures. For a given system, the higher the temperature the faster the reaction and the lower the molecular weight.

#### *2.1.1.2 Ziegler Process*

This type of polymerization is referred to as co-ordination polymerization since the mechanism involves a catalyst monomer, co-ordination complex or some other directing catalysts are formed by the interaction of the alkyls of Groups I-III metals with halides and other derivatives of transition metals in group IV-VIII of the periodic Table. Ethylene is fed under low pressure into the reactor which contains liquid hydrocarbon to act as diluent. Reaction is carried out at some temperatures below 100°C (typically 70°C) in the absence of oxygen and water, both of which reduce the effectiveness of the catalyst. The catalyst remains suspended and the polymer as it is formed which progressively thickens as the reaction proceeds. The Ziegler polymers are intermediate in density (about 0.945 g/cm<sup>3</sup>) between the high pressure polyethylenes. A range of molecular weights may be obtained by varying the Al-Ti ratio in the catalyst, by introducing hydrogen as a chain transfer agent and by varying the reaction temperature.

#### *2.1.1.3 The Phillips process*

Ethylene, dissolved in a liquid hydrocarbon such as cyclohexane, is polymerized by a supported metal oxide catalyst at about 130°C-160°C and at about 200-500 lb.in<sup>-2</sup>

pressure. The solvent serves to dissolve polymer as it is formed and as a heat transfer medium but is otherwise inert. The preferred catalyst is one which contains 5% of chromium oxides, mainly  $\text{CrO}_2$ , on a finely divided silica-alumina catalyst (75-90% silica) and which has been activated by heating to about  $250^\circ\text{C}$ . Polymers ranging in melt flow index less than 0.1 to greater than 600 can be obtained by this process but commercial products have a melt flow index of only 0.2-5 and have the highest density of any commercial polyethylenes (about  $0.96\text{ g/cm}^3$ ). The polymerization mechanism is largely unknown but no doubt occurs at or near the catalyst surface where monomer molecules are both concentrated and specifically oriented so that highly stereospecific polymers are obtained. It is found that the molecular weight of the product is critically dependent on temperature and in a typical process there is a forty-fold increase in melt flow index, and a corresponding decrease in molecular weight, in raising the polymerization temperature from  $140^\circ\text{C}$  to just over  $170^\circ\text{C}$ . Above  $400\text{ lb.in}^{-2}$  the reaction pressure has little effect on either molecular weight or polymer yield but at lower pressures there is a marked decrease in yield and a measurable decrease in molecular weight. The catalyst activation temperature also has an effect on both yield and molecular weight.

#### 2.1.1.4 *Standard Oil Company (Indiana) Process*

This process has many similarities to the Phillips process and is based on the use of a supported transition metal oxide in combination with a promoter. Reaction temperatures are of the order of  $230^\circ\text{C}$ - $270^\circ\text{C}$  and pressures of 40-80 atm. Molybdenum oxide is a catalyst that figures in the literature and promoters include sodium and calcium as either metals or as hydrides. The reaction is carried out in a hydrocarbon solvent. The products of the process have a density of about  $0.96\text{ g/cm}^3$ , similar to the Phillips polymers. Another similarity between the processes is the marked effect of temperature on average molecular weight. The process is worked by the Furukawa Company of Japan and the product marketed as Staflen.

## 2.2 Polypropylene (PP)

Polyethylene would lead after the war to an improved material, polypropylene (PP), which was discovered in the early 1950s. It is common in modern science and technology that the growth of the general body of knowledge can lead to the same inventions in different places at about the same time, but polypropylene was an extreme case of this phenomenon, being separately invented about nine times. It was a patent attorney's dream scenario, and litigation wasn't resolved until 1989. Polypropylene managed to survive the legal process, and two American chemists working for Phillips Petroleum of the Netherlands, Paul Hogan and Robert Banks, are now generally credited as the "official" inventors of the material.

Resins are a general class of thermoplastics produced from propylene gas. Propylene gas is derived from the cracking of natural gas feedstocks or petroleum by-products. Under broad ranges of pressures and temperatures, propylene generally polymerizes to form very long polymer chains. However, to make polypropylene resins with controlled configurations of molecules (tacticity) at reasonably acceptable commercial rates, special catalysts are required. By utilizing techniques such as multiple reactor configurations, polymerizing other gases such as ethylene or butene in conjunction with propylene to form copolymers, using special additives to control crystallinity, etc., different types of PP resins can be produced. The ability to produce so many variations of a basic material permits the manufacturer to tailor PP resins for diverse applications, such as packaging films; clear, rigid food containers; appliance parts; automotive bumper fascia and batteries; medical syringes; etc.

### 2.2.1 Polymerization of Polypropylene

PP resins are generally produced in large, continuous reactor systems operating in a slurry, bulk or gas phase mode. In all cases, the resultant PP products are pelletized on compounding extruders where additives such as antioxidants, processing aids, etc. are incorporated. A slurry reactor is usually a large diameter pipe in the form of a loop that is filled with a non-reactive diluent such as isobutane. Propylene and catalyst are



fed into the reactor. As the PP is produced, it forms into small crumbs which are insoluble in the diluent and circulate as slurry. A portion of this slurry is continuously removed and the PP crumbs are separated, dried and conveyed to the extrusion area. A bulk system operates in a similar fashion except liquefied propylene is used as the diluent for the slurry. The use of propylene is advantageous because there is no need to separate any unreacted propylene from the diluent. In the gas phase process, no liquid is used and the reaction takes place in a fluidized or mechanically agitated bed of polypropylene powder. All liquid separation and treating steps are essentially eliminated in this process.

## 2.2.2 Classifications of Polypropylene

Following is a review of the four basic categories of PP resins, how they are produced, and their key properties.

### 2.2.2.1 *Polypropylene Homopolymers*

Only propylene is used in the reaction producing PP homopolymers and usually they are made on a single reactor system. PP homopolymers exhibit high stiffness, high temperature resistance and excellent chemical resistance. End products usually have a hard surface that resists scratching and staining. PP homopolymers are available in a wide range of melt flow rates and are used to produce, for example, oriented film, thermoformed deli containers, appliance parts, caps and closures, monofilaments, non-woven cloth and carpet fibers. PP homopolymers do not have good impact strength at low temperatures, so homopolymers are not generally suitable for applications exposed to temperatures below normal refrigeration.

### 2.2.2.2 *Random Copolymers*

One way to improve the impact strength of PP at low temperatures is to add a second component, ethylene, in the reactor step. The resulting PP product is called a random copolymer. The addition of the second component reduces the crystallinity of

the PP to some extent and provides two benefits: marginal impact improvement at lower temperatures and clarity. The amount of ethylene added is usually two-to-four percent.

In the resulting polymer, the ethylene molecules are randomly inserted along the polypropylene chain. These polymer chains are more flexible so their flexural modulus (stiffness) is reduced but impact resistance improves slightly at room temperature and below. Such PP random copolymer products are used in applications such as see-through freezer storage containers, syrup and household chemical bottles, VCR cases, tackle box components and storage boxes. If special additives called clarifiers are also added, the sizes of the crystallite areas in the polymer are reduced and clarity, gloss and stiffness are enhanced. Clarified random copolymers are commonly used for food storage containers and bottles. Although not as stiff as homopolymers, random copolymers can still be used for hot fill applications.

### 2.2.2.3 *Impact Copolymers*

PP impact copolymers provide the highest level of impact strength, especially at sub-ambient conditions. These materials are manufactured in a two-reactor system, operating in series. In the first reactor, PP homopolymer is produced. Instead of transferring this product to extrusion compounding, it is conveyed to a second reactor. This also contains a high concentration of ethylene. The ethylene, in conjunction with the residual propylene left over from the first reactor, copolymerizes to form an ethylene-propylene rubber (EPR). The resultant product has two distinct phases: a continuous, rigid homopolymer matrix and a finely dispersed phase of EPR particles. This rubber phase absorbs and disperses the energy of any impact load to prevent part failure while overall the rigid homopolymer matrix maintains stiffness. Although impact modification can be done by mechanically mixing rubber into a PP homopolymer, it is not possible to achieve either the level of dispersion or a small enough rubber particle size (about five microns) to obtain the maximum rubber efficiency that can be achieved by in-reactor synthesis. By carefully adjusting the amount and composition of the EPR, a wide range of impact/stiffness combinations can be produced. Impact copolymers are used in diverse applications including medical waste bags, automotive batteries and heavy-duty

tool and tackle boxes. Impact copolymers are also used as the base materials for producing filled and reinforced compounds for many automotive structural applications. Because these materials are composed of two distinct phases, impact copolymers tend to be translucent to opaque.

#### 2.2.2.4 *Olefinic Thermoplastic Elastomers*

These products, often referred to as TPOs, are a relatively new PP development. Historically, the highest rubber content that could be incorporated into an impact copolymer in the second reactor was about 20-25%. With the advent of new catalyst and process technologies, these capabilities have widened considerably and some products have been developed with rubber content of 50% or more. Such high rubber levels result in products with excellent impact strength even at temperatures as low as  $-30^{\circ}\text{C}$ . Although some amount of stiffness is lost, these materials can still be used in material handling crates, highway dividers, etc. However, the largest application for TPOs is filled and reinforced compounds which are replacing many of the more expensive engineering thermoplastics in automotive and appliance applications, such as paintable bumper fascia and interior panels.

### 2.3 Extrusion Process (Morton-Jones, 1989: 74-77)

The extrusion is a unique process in that it is continuous. All others process start and stop as each part is molded. Once the extruder is set up, a continuous product is made. Extruded products include film, sheet, rod and pipe. The unit consists of a heated cylinder or barrel, screw, hopper, and die. The die is also heated. Temperatures for extrusion range from  $165^{\circ}\text{C}$  to  $316^{\circ}\text{C}$  depending on the plastic. The extrusion process comprises the forcing of a plastic or molten material through a shaped die by pressure. The process has been used for many years for metal such as aluminum, which flow plastically under deforming pressure. In the modern process, however, screws are used to progress the polymer in the molten or rubbery state along the barrel of the machine. The most widely used type is the single screw machine and Figure 2.3 shows the main feature of this type of extruder.

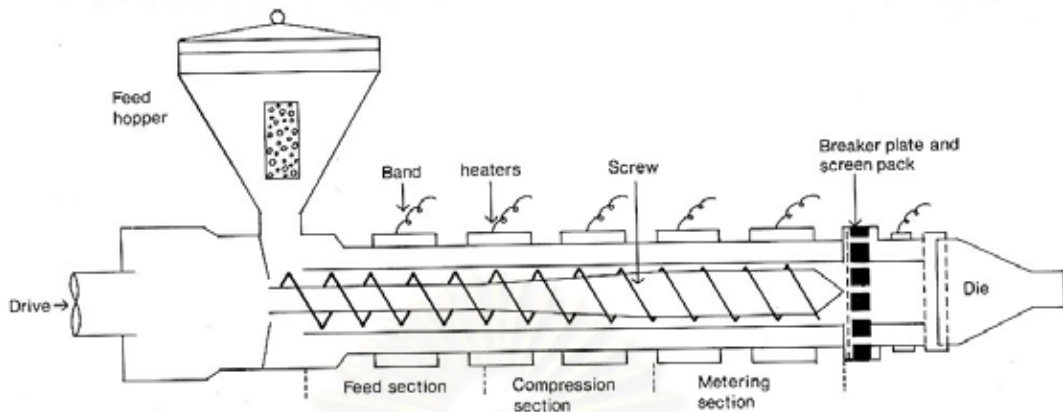


Figure 2.3 Main features of a single screw extruder

Twin screw extruders are used where superior mixing or conveying is important. The machines consist of an Archimedian screw fitting closely in a cylindrical barrel, with just sufficient clearance to allow its rotation. Solid polymer is fed in at one end and the profiled molten extrudate emerges from the other. The polymer melts and homogenizes.

### 2.3.1 Features of a Single Screw Extruder

The screw of an extruder has one or two flights spiraling along its length. The diameter to the outside of the flight is constant along the length to allow the close fit in the barrel. The core is of varying diameter and so the spiraling channel varies in depth. In general, the channel depth decreases from feed end to die end shown in Figure 2.4.

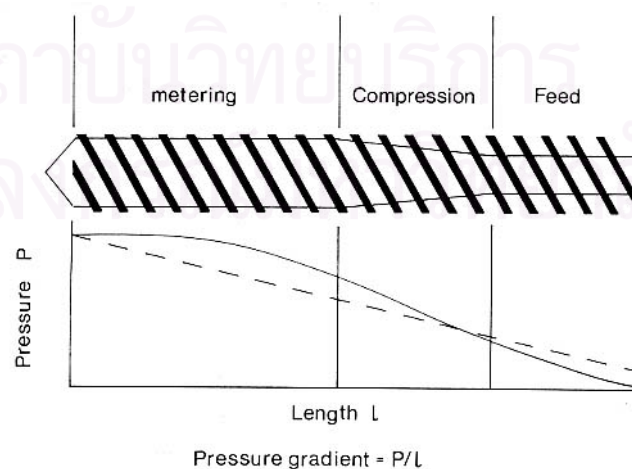


Figure 2.4 Zones in a single screw extruder

A sequence of the decreasing channel depth is increasing pressure along the extruder and there are three zones, whose functions are as follows. There is also the die zone, which will be examined

Zones in an extruder are as follows:

#### 2.3.1.1 Feed zone

In the first zone, usually termed the feed zone, the function is to preheat the polymer and convey it to the subsequent zones. The screw depth is constant and the length of this zone is such as to ensure a correct rate of feed forward.

#### 2.3.1.2 Compression zone

The second zone has decreasing channel depth. There are several functions for this zone or transition zone. Firstly, it expels air trapped between the original granules; secondly, heat transfer from the heated barrel walls is improved as the material thickness decreases; thirdly, the density change during melting is accommodated. There is variation in the ideal design for each polymer type that is shown in Figure 2.5.



Figure 2.5 Variations in screw design

#### 2.3.1.3 Metering zone

Once again we find constant screw depth. The function is to homogenize the melt and hence to the die region material which is of homogeneous quality at constant temperature and pressure.

#### 2.3.1.4 *The die zone*

The final zone of an extruder is the die zone, which terminates in the die itself. Located in this region is the screen pack (Figure 2.3).

This usually comprises a perforated steel plate called the breaker plate and a sieve pack of two or three layers of wire gauze on its upstream side. The breaker plate has three functions:

- 1) to sieve out extraneous material, e.g. ungelled polymer, dirt, foreign bodies,
- 2) to allow head pressure to develop by providing a resistance for the pumping action of the metering zone,
- 3) to remove turning memory from the melt.

#### 2.3.2 Flow Mechanisms [Morton-Jones, 1989: 82-84]

We have seen the main physical features of a single extruder. The machine functions melt and convey the polymer down its length as shown in this section.

##### 2.3.2.1 *Melting*

As the polymer is conveyed along the screw, a thin film melts at the barrel wall. This usually by means of conducted heat from the barrel heaters, but could be frictional. The screw scrapes off the melted film as it rotates. The molten polymer moves down the front face of the flight to the core and then sweeps up again to establish a rotary motion in front of the leading edge of the flight. Other solid granules or parts of the compacted slug of polymer are swept into the forming melt pool. The process is progressive until all the polymers are melted.

##### 2.3.2.2 *Conveying*

To understand the conveying mechanism, consider two extremes.

- 4) The material sticks to the screw and slips on the barrel. Under these conditions the screw and material would simply rotate as a solid cylinder and there would be no transport.

5) The material resists rotation in the barrel and slips on the screw. It will now tend to be transported axially, like a normal, deep-channeled, solids-conveying Archimedian screw.

In practice, there is friction with both screw and barrel, and this leads to the principal transport mechanism, drag flow. This is literally the dragging along by the screw of the melt as the result of the frictional forces. And is the equivalent to the viscous drag between stationary and moving plates separated by a viscous medium. It constitutes the output component for the extruder. It is opposed by the pressure flow component, which is caused by the pressure gradient along the extruder. As we have seen, there is high pressure at the output end, low at the feed end and this pressure gradient opposes the drag flow. The final component in the flow pattern is leak flow. There is a finite space between screw and barrel through which material can leak backwards. This is also a pressure-driven flow and of course it also opposes drag flow. Thus the total flow is the sum of these components.

$$\text{Total flow} = \text{drag flow} - \text{pressure flow} - \text{leak flow} \quad (2.1)$$

### 2.3.2.3 Heating and Cooling

In high-speed machines, virtually all the heating is from shearing of the viscous melt. Some heat derives from this source and some from the barrel heaters. There are also coolers, usually fans to remove excess heat. The whole system is controlled thermostatically to give precise control of melt temperature. The length of the machine is divided into three or four sections to allow variation of temperature for optimum processing. The practical running condition may be regarded as lying between the extremes of adiabatic running, when there would be only heat from viscous dissipation, and isothermal running, when the temperature at all points would be the same, with heat being supplied by heaters or removed by coolers to compensate for changes in melt temperature.

## 2.4 Injection Process

The injection molding is the most important plastic processing method. Over 60% of all thermoplastics are injection molded. It is a very fast high production process. Thermosets are now being injection molded. Typical injection molded products include pails, refrigerator containers, and chair seats and backs. Disposable products such as plastic cups, knives, forks, and spoons, are injection molded. Radio and television cabinets and control knobs are also injection molded. Injection molding is used to mold many furniture parts using high impact polystyrene. The fronts of drawers and door panels for dining room and bedroom furniture are injection molded by many companies. Mirror and picture frames are also injection molded. The mold is engraved with a wood grain pattern. The molded part is then finished to match the rest of the furniture. Plastics have the advantages of being less expensive. Also, plastics do not warp or split as wood sometimes does. Two injection units can be used at the same time to mold two-color parts such as adding machine and typewriter keys. Foams can also be injection molded for structural parts in furniture. An injection molder is made up of a barrel that is heated to the desired temperature by electrical band heaters. The plastic is stored in a hopper that feeds plastic to barrel. Cold water is circulated around the base of the hopper so that the plastic does not melt. If the plastic were to melt, it would clog the hopper opening. There are two basic types of injection molders. The old type is called a plunger or a ram injection molder. The newer type is called a reciprocating screw injection molder. The plunger or the screw moves the plastic through the barrel and out the nozzle into the closed mold.

### 2.4.1 The Injection Unit

The injection unit is essentially a single screw extruder. The injection unit is the plasticizing part of the process. The polymer response is the same, and screw designs, barrel heating, etc., are very similar. The one major difference is that the screw can reciprocate, piston-like, within the barrel during the injection part of the production cycle. During the plasticizing phase, the output end is sealed by a valve and the screw



accumulates a reservoir or shot of melt in front of itself by moving backwards against the head pressure. When this phase is complete, the sealing valve opens, the screw stops rotating and pressure is applied to it so that it becomes a ram or piston which forces the accumulated melt through the connecting nozzle into mold, contained in the clamp unit.

#### 2.4.2 The Clamp Unit

The clamping force must be great enough to resist the force generated by the melt as it is injected. The pressure in this melt can be around 145 Mpa, so that for moldings with a large projected area the force required can be considerable.

#### 2.4.3 The Mold or Tool

The mold is mechanically fastened in the clamp unit, but is interchangeable to allow different products to be molded. The essential features of a mold such as:

- 6) the cavity or impression,
- 7) the channels, along which the melt flows as it is injected,
- 8) cooling channel, through which cooling water is pumped to remove the heat of the melt,
- 9) ejector pins, which remove the molding from the cavity.

### 2.5 Polymer Degradation

The term polymer degradation is used to denote changes in physical properties caused by chemical reactions involving bond scission in the backbone of the macromolecule. (Schnabel, 1981: 14) In linear polymers, these chemical reactions lead to a reduction in molecular weight, i.e. to a diminution of chain length as shown in Figure 2.6.

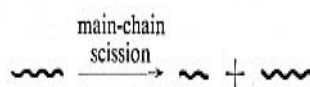


Figure 2.6 Diminution of chain length

The definition of polymer degradation is extended to include changes of physical properties, caused not only by chemical but also by physical reactions, involving the breakdown of higher ordered structures. The term polymer degradation involves a deterioration in the functionality of polymeric materials, which in the case of biopolymers is called denaturation. The chemical aspects of polymer degradation are not only caused by bond scissions in the polymer backbone, but also by simultaneously occurring chemical reactions in pendant groups of linear polymers, affect the physical properties only to a minor extent relative to reactions in the backbone. Intermolecular cross-linking, i.e. the formation of new chemical bonds between individual macromolecules, may be considered the opposite of degradation as it leads to an increase in molecular size and, at higher conversions, to certain kinds of spatial networks with characteristic physical properties.

#### 2.5.1 Factors and Stresses Causing Degradation

Macromolecules are composed of monomeric units, which are joined by chemical bonds to each other. (Schnabel, 1981: 13-14) The monomeric units contain chemical bonds, which either are in the main chain of the macromolecule or connect various atoms or side groups to it. Side groups, if they are present, contain additional chemical bonds. All of these bonds may be reaction sites in polymer degradation, and various energy sources may be effective in supplying the energy necessary to break the bonds. The bond energies are manifold and depend not only on the kind of atoms connected by the bond but also on the chemical and physical characteristics surrounding the bond. The dissociation energies of chemical bonds in common polymers range from about 65 kcal/mol (C-Cl) to 108 kcal/mol (C-F) with carbon-carbon bonds in the middle (75-85 kcal/mol). The most important types of energy that cause polymer degradation are heat, mechanical energy, and radiation. Thermal and mechanical degradation of polymers may occur during thermomechanical processing. An extreme case of heat damage is burning. The flammability and combustion behavior of polymers are very important in many applications. A typical example of pure mechanical destruction of a polymeric material is grinding, although the evolved heat

may play a role even in this case. The most common form of radiant energy which causes degradation is that of the UV component of sunlight; the energy of a photon with  $\lambda = 300 \text{ nm}$  is about 95 kcal/mol, which is higher than most bond dissociation energies in polymers. In special applications, e.g., polymers used in x-ray laboratories in hospitals or in plastic parts for aerospace applications, nuclear radiation may cause degradation. Not only is the role of temperature important when the heat necessary for bond dissociation is supplied by thermal motion of the atoms, it can also activate various chemical and biological processes. Reactions of polymers with oxygen and moisture, generally present in various applications, are very important in polymer degradation. Ozone degradation of elastomers is of the utmost importance in the rubber industry. Recently, the stability of polymers in the presence of pollutant gases such as sulfur dioxide and nitrogen dioxide has aroused interest. The factors are not separated; various combinations of damaging components (e.g., a hammer blow), but they may also act for a much extended time period. The behavior of the same polymer under impact and fatigue conditions may differ to a great extent; this is also true when other types of stress, not just mechanical, are involved. As a result of degradation processes, initiated and completed by the above factors or their combination, the internal properties as well as the external appearance of the polymers may change. Chain-scission and cross-linking lead to a change of molecular weight distribution. Oxidation and other chemical reactions, in the side chains too, cause changes in chemical composition result in discoloration. These alternations cause the deterioration of mechanical and other important properties. As a result, the material loses its value and becomes a useless waste.

#### 2.5.2 Chemical Degradation (Schnabel, 1983: 178-179)

Commonly, the rate of chemical reaction is depending on temperature, which implies that thermal and chemical process. Thermal degradation can be distinguished from chemical degradation, by restricting the former term to those processes, which are initiated by heating, i.e. without the addition of another compound. All polymers contain

small amounts of low molecular weight compounds (impurities, plasticizers etc.) Which might undergo chemical reactions with the macromolecules as the temperature is increased. Chemical reaction leads to main chain scission and/or deterioration of physical properties. Consequently, emphasis will be given to aspects concerning the stability of polymers against chemicals. Polymers containing unsaturated carbon-carbon bonds are also of interest, because they are susceptible to metathesis reactions or reactions with ozone. Reactions of polymers with molecular oxygen are of general importance because oxygen is ubiquitous. Therefore, oxidative processes cause problems not only in outdoor exposures of plastics but also in processing. Oxidative degradation proceeds according to free radical chain reactions (autoxidation) initiated by UV-light. Recently, air pollution has become a worldwide problem. The behavior of plastics towards pollutant gases ( $\text{NO}_2$  and  $\text{SO}_2$ ) has gained importance and has become the subject of investigations. The importance of the stability of polymers against solvents has to be considered. Solid polymeric articles change or lose shape or deteriorate on immersion into liquid chemicals. This phenomenon might be caused by chemical reactions. The result of a physical process consists of a strong interaction between the polymer and the liquid. Under the influence of this interaction, the polymer dissolves or swells to a limited degree but remains chemically intact. The term chemical stability is used in a broad sense covering both chemical and physical interaction of low molecular weight compounds with polymers. Another interesting phenomenon concerns the fact that many polymers consist of amorphous and crystalline fractions. For certain chemical reactions, e.g. hydrolysis, the crystalline regions have been found impervious to chemical agents. Thus, the amorphous fraction of the polymer is attacked selectively, a fact capable of being utilized, for instance, for analytical purposes (determination of the degree of crystallinity).

### 2.5.3 Mechanical Degradation (Schnabel, 1983: 64-74)

Mechanical Degradation comprises a large field covering fracture phenomena as well as chemical changes induced by mechanical stress. Because of macromolecular chemical structure, plastics possess in many respects rather unique

physical properties that account for their utilization as raw materials for various purposes. The plastic engineer has to be aware of the loading capacity and of the fact that under permanent mechanical stress plastic materials might exhibit a behavior quite different from that encountered with metal and other inorganic raw materials. In the past, sudden breakdown or fatigue phenomena resulting in morphological changes (deformations, crazing and cracks) have been treated predominantly on the basis of the physical nature of the development of defects. Only quite was attention drawn more generally to the chemical changes induced in polymers under the influence of mechanical stress. The influences of mechanical stress low molecular weight organic materials generally exhibit a different behavior to polymers. Normally, they do not undergo chemical changes if subjected to stress. Assemblies of low molecular weight molecules respond to applied stress by loosening intermolecular (physical) bonds resulting, in a deformation of the shape of the specimen and, microscopically, in a displacement of molecules. Thus, under the influence of shearing forces, intermolecular interactions between molecules at certain sites in a specimen are disrupted and new interactions become operative after the displacement. Cracking crystals or amorphous specimens of low molecular weight compounds does not lead to the formation of free radicals, indicative for the scission of chemical bonds. On the other hand, free radicals are generally detected in polymers after mechanical treatment indicating ruptures of chemical bonds. From this example it is evident that the mechanical degradation of polymers has to be looked upon not only from the viewpoint of the physicist or the plastic engineer but also from the sight of the chemist.

The mechanical of chain scission bond are shown in Figure 2.7.

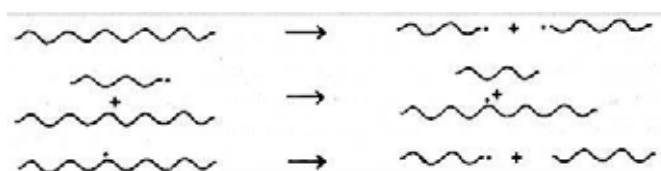


Figure 2.7 Mechanical of chain scission bond

#### 2.5.4 Thermal Degradation (Schnabel, 1983: 25-294)

Organic macromolecules are stable only below a certain limiting temperature range from 100°C to 200°C. If the temperature is increased to 1,000°C or higher, organic molecules decompose into small fragments (free radicals, free ions, H<sub>2</sub>, etc.). Molecules are composed of atoms linked together by covalent bonds. Thermal degradation came from breaking covalent bond in polymer chain that has energy breaking primary bond at 25°C in the range 300 – 900 kJ/mol. In the case of heat energy in atmosphere that have mean about 2.4 kJ / mol, so breaking bond at room temperature but the temperature will raise to point that indicate oxidation reaction so to break bond at lower temperature that we expect. The chemical change due to the braking bond in the main of polymer chain and beside the main of polymer chain, so the molecular weight decrease and gave the light molecular weight or occurring the ring and cross-linking so the molecular weight increase. The picture of reactions occuring during thermal degradation of polymers is shown in Figure 2.8.

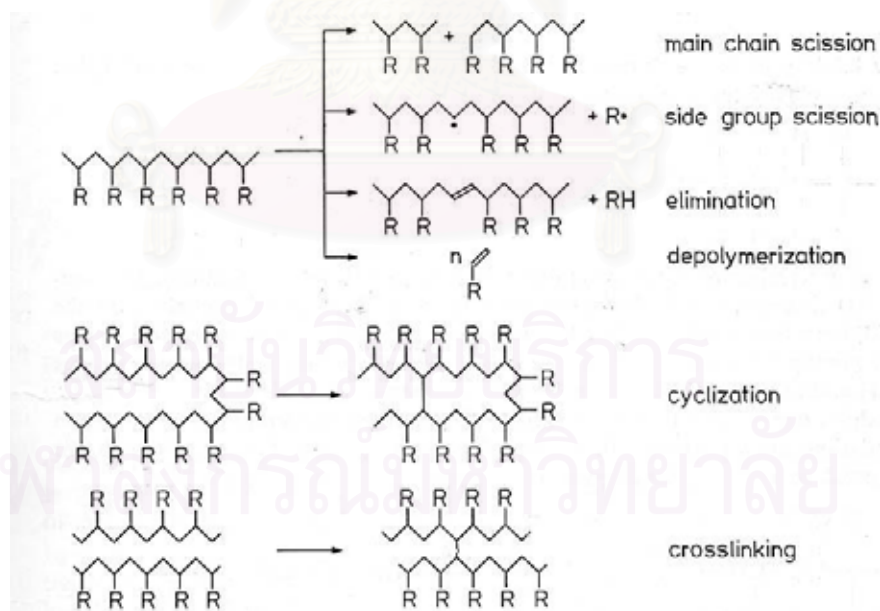
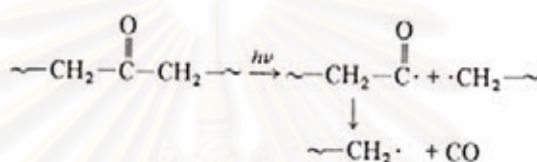


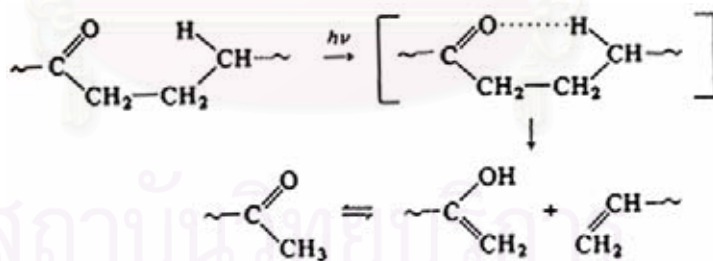
Figure 2.8 Thermal degradation of polymer

### 2.5.5 Oxidative Degradation (Kelen, 1983: 142-143)

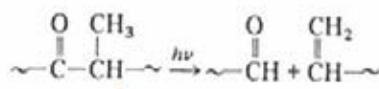
The role of carbonyl groups in polymer oxidation is of great importance because once they have been formed they absorb UV light readily, hence, excitation to singlet and triplet state is easy. The excited carbonyl groups decompose via Norrish reactions of types I, II and III. The norrish -I reactions is a radical cleavage of the bond between the carbonyl group and the  $\alpha$ -carbon atom ( $\alpha$ -scission), and is usually followed by the formation of carbon monoxide:



The Norrish-II reaction is a nonradical scission which occurs through the formation of a six-membered cyclic intermediate. Abstraction of a hydrogen from the  $\gamma$ -carbon atom results in decomposition by  $\beta$ -scission to an olefin and an alcohol or ketone. For example, in the case of polyethylene, a terminal double bond and an enol/ketone end group are formed.



The Norrish-III reaction is also a nonradical chain scission; however, it involves the transfer of a  $\beta$ -hydrogen atom and leads to the formation of an olefin and an aldehyde.



## 2.6 Thermal decomposition

Thermal decomposition in the means of the American Society for Testing and Materials (ASTM) is a process of extensive chemical species change caused by heat, but thermal degradation is a process where by the action of heat or elevated temperature on a material, product, or assembly causes a loss of physical, mechanical or electrical properties. In term of fire, the important change is thermal decomposition; the chemical decomposition generates gaseous fuel vapors or volatiles. The processes can be a continuous feedback loop if the material continues burning. In the case, heat transferred to the polymer causes the generation of flammable volatiles; these volatiles react with the oxygen in the air above the polymer to generate heat, and a part of this heat is transferred back to the polymer to continue the process.

The chemical processes are responsible for the generation of flammable volatiles while physical changes can markedly alter the decomposition characteristics of a material. The gasification of polymers is complicated than that of flammable liquids.

The liquid evaporates at a rate required to maintain the equilibrium vapor pressure above the liquid. In the case of polymeric materials, the original material itself is essentially involatile and the quite large molecules must be broken down into smaller molecules. In most cases, a solid polymer breaks down into a smaller molecular fragments made up of a number of different chemical species. Hence, each of the fragments has a different equilibrium vapor pressure. The lighter of the molecular fragments will vaporize immediately upon their creation while other heavier molecules will remain in the condensed phase (solid or liquid) for some time. While remaining in the condensed phase, these heavier molecules may undergo further decomposition to lighter fragments. Some polymers break down completely so that virtually no solid residue remains; however, not all the original fuel becomes fuel vapors since solid residues are left behind. These residues can be carbonaceous (char), inorganic (originating from heteroatoms contained in the original polymer, either within the structure or as a result of additive incorporations), or a combination of both. When thermal decomposition of deeper layers of such a material continues, the volatiles



produced must pass through the char above them to reach the surface. During this travel, the hot char may cause secondary reactions in the volatiles. Carbonaceous chars can be in tumescent layers, when appropriately formed, which slow down further thermal decomposition considerably.

## 2.7 Detection of Polymer Degradation (Schnabel, 1983: 20-23)

### 2.7.1 Changes in Molecular Size

The methods of investigating polymer degradation are as numerous as the processes themselves. In most cases we must use accelerated or intensified testing methods because the natural processes are slower than the synthetic processes. We simulate the factors causing degradation and then apply them in an intensified manner. When we study oxidative degradation of polyolefins (a slow process under real conditions, e.g., by storing the material at room temperature in air). To follow the process to observe the response of the polymer to the above attacks, we must analyze the system as many as possible. Among the various methods for the detection of chemical changes, those based on molecular size determinations play an eminent role, as far as linear (non-crosslinked) polymers are concerned. Even low conversions yield significant changes of the average molecular weight, if the initial molecular weight is sufficiently high. The same holds for intermolecular cross-linking, a process occurring, for example, in many cases where lateral macroradicals are formed:



Figure 2.9 Intermolecular cross-linking

Molecular weight determinations have been carried out, therefore, rather frequently in order to evidence chemical reactions in the main chains or at side groups of linear polymers and to elucidate reaction mechanisms. Since synthetic polymers usually consist of a mixture of chemically identical macromolecules of different size, the

molecular size-or molecular weight-distribution (MWD) are important properties, which characterize a polymer. Frequently the MWD is altered upon main-chain rupture and/or cross-linking, hence MWD changes have been treated theoretically by several authors, especially with respect to random main-chain scission in linear polymers in the absence of cross-linking. Some of the results pertaining to changes of MWs and MWDs and their value in the determination of scission yields will be presented here. In this connection, it is important to note that MWD determinations can be readily carried out with the aid of gel permeation chromatography (GPC). If a linear polymer, having an initial unimodal MWD, undergoes random main-chain scission, the number average degree of polymerization,  $u_1$ , decreases with increasing degree of degradation,  $\alpha$  according to this equation.

$$\frac{u_1}{u_{1,0}} = \frac{1}{1 + \alpha} \quad (2.2)$$

Where  $\alpha$  denotes the number of scissions per initial molecule and  $u_{1,0}$  the initial number average degree of polymerization. For the change in the weight average degree of polymerization,  $u_2$ , as a function of  $\alpha$ , Equation 2.3 holds.

$$\frac{u_2}{u_{2,0}} = \frac{2}{\alpha \sigma_0} \left\{ 1 - \frac{1}{\alpha} \left[ 1 - \int_0^{\infty} \frac{\omega(y) e^{-\tau y} dy}{\frac{y}{u_{1,0}}} \right] \right\} \quad (2.3)$$

where

$\sigma_0 = \frac{u_{2,0}}{u_{1,0}}$  : A parameter characterizing the breadth of unimodal MWDs

$\omega(y) = \frac{yn(y)}{u_{1,0}}$  : Weight fraction of y-mers initially present

$\tau = \frac{\alpha}{u_{1,0}}$  : Number of scissions per base unit

Equation 2.2 and 2.3 hold for the case of  $u_{1,0} \gg 1 \gg \tau$ .

MWDs of the Schulz-Zimm type are frequently considered. In this case the weight fraction  $\omega(y)$  is expressed by Equation 2.4.

$$\omega(y) = \nu^{(b+1)} y^b \frac{e^{-\nu y}}{\Gamma(b+1)} \quad (2.4)$$

The parameter  $\nu$  is characterized by the relationships  $u_1 = \frac{b}{\nu}$  and  $u_2 = \frac{b+1}{\nu}$  with  $b = \frac{1}{\sigma-1}$ .

For a MWD of Schulz-Zimm type, one obtains from Equation 2.5.

$$\frac{u_2}{u_{2,0}} = \frac{2}{\alpha \sigma_0} \left\{ 1 + \frac{1}{\alpha} \left[ 1 + \frac{\alpha}{b_0} \right]^{-b_0} - 1 \right\} \quad (2.5)$$

$\sigma$  depends on  $\alpha$  as given by Equation 2.6.

$$\sigma = \frac{2(1+\alpha)}{\alpha} \left\{ 1 - \frac{1}{\alpha} \left[ 1 - \frac{1}{\left(1 + \frac{\alpha}{b_0}\right)^{b_0}} \right] \right\} \quad (2.6)$$

Criteria for random main-chain scission are derived both from Equations 2.2 and 2.5, and from 2.6. Plots representing the relative change  $\frac{u_2}{u_{2,0}}$  as a function of the relative change  $\frac{u_1}{u_{1,0}}$  at various values of  $\sigma_0$ . By comparison of the calculated with the experimentally determined molecular weight change it can, therefore, be deduced, whether or not random main-chain scission had occurred. Another criterion for random scission is based on the fact, that, independent of  $\sigma_0$ ,  $\sigma$  approaches a limiting value of 2 with increasing  $\alpha$ .  $\sigma$  is independent of  $\alpha$  and remains constant during random main-chain-scission ( $\sigma = \sigma_0 = 2$ ), as is evident from Equation (2.6). With respect to the determination of yields of main-chain scission, it is interesting to note, that for  $b_0 = 1$ , Equation 2.6 can be simplified to

$$\frac{u_1}{u_{1,0}} = \frac{1}{1+\alpha} \quad (2.7)$$

### 2.7.2 Analytical Techniques Applied in polymer Degradation [Schnabel, 1981: 23]

Apart from methods for MW and MWD-determinations, which are powerful in detecting degradation in linear soluble polymers, there is the wealth of conventional analytical methods, which are usually also applied in order to demonstrate chemical changes in polymers. An important drawback, in comparison with low molecular weight compounds, is the fact that the separation of reacted from unreacted macromolecules is usually impossible. As most analytical investigations are performed on bulk polymers, which are usually converted by degradation to a very small extent only, this drawback is limiting. A somewhat different situation is encountered, however, when gaseous low molecular weight products are formed in the degradation process. These products separate from the polymer specimen and can therefore, are easily analyzed (qualitatively and quantitatively). Indeed, volatilization analysis has been frequently applied, especially in thermal, photochemical and radiation-chemical degradations. Sophisticated techniques have been developed to collect, fractionate and analyze volatile products. Systems for volatilization analyses consist of a vacuum line, to which a series of cold traps and pressure gauges are connected in order to collect different products. For separation and identification, gas chromatography and mass spectrometry are used. Commonly, volatilization analysis yields valuable information about chemical reactions, which cause decomposition in pendent groups, and this technique contributes, therefore, frequently to the elucidation of degradation mechanisms. The importance of volatilization analysis is, of course, outstanding in cases where the formation of gaseous products is the dominating chemical process, such as in depolymerizations (unzipping) and plasma etching. As far as chemical changes in bulk polymers are concerned, spectroscopic methods, such as infrared (IR) and ultraviolet (UV) absorption spectroscopy, are used to detect the formation or disappearance of chromophoric groups. Nuclear magnetic resonance (NMR) techniques have proved helpful to analyze structural changes. With regard to the detection of reactive intermediates, prominence must be given to electron spin resonance (ESR) spectroscopy. There are various other analytical techniques, such as

differential thermal analysis (DTA) and differential scanning calorimetry (DSC) which are important in special fields of degradation, for example, DTA and DSC are used in studies of thermal degradation.

### 2.7.3 Yellowing Phenomena (Berns, 2000:70)

Because the presence of small amounts of yellowness in nearly white (or nearly colorless) samples is both common and, usually, objectionable, considerable attention has been paid to devising uniform yellowness scales. The ASTM (ASTM E313) has adopted a yellowness scale based on CIE color coordinates for the CIE 1931 observer and illuminant C. These scales correlate with visual perception only for colors seen as yellow or blue; in the latter case, the yellowness index is a negative number. They should never be used to describe colors that are visibly reddish or greenish.

A yellowness index based on CIE tristimulus values for illuminant C and the 1931 standard observer (ASTM E 313) is given by

$$YI = 100 \times \frac{1.2769X - 1.0592Y}{Y} \quad (2.8)$$

## 2.8 Recycling Plastics (Immediate Technology Development Group, 2004)

In western countries, plastic consumption has grown at a tremendous rate over the past two or three decades. In the consumer societies of Europe and America, scarce petroleum resources are used for producing an enormous variety of plastics for an even wider variety of products. Many of the applications are for products with a life-cycle of less than one year and then the vast majority of these plastics are then discarded. In most instances reclamation of this plastic waste is simply not economically viable. In industry (the automotive industry for example) there is a growing move towards reuse and reprocessing of plastics for economic, as well as environmental reasons, with many praiseworthy examples of companies developing technologies and strategies for recycling of plastics. Not only is plastic made from a non-renewable resource, but it is generally non-biodegradable (or the biodegradation process is very

slow). This means that plastic litter is often the most objectionable kind of litter and will be visible for weeks or months, and waste will sit in landfill sites for years without degrading. Although there is also a rapid growth in plastic consumption in the developing world, plastic consumption per capita in developing countries is much lower than in the industrialised countries. These plastics are, however, often produced from expensive imported raw materials. There is a much wider scope for recycling in developing countries due to several factors.

### 2.8.1 Plastics for Recycling

Not all plastics are recyclable. There are 4 types of plastic, which are commonly recycled:

- polyethylene (PE) - both high density and low-density polyethylene
- polypropylene (PP)
- polystyrene (PS)
- polyvinyl chloride (PVC)

A common problem with recycling plastics is that plastics are often made up of more than one kind of polymers or there may be some sort of fiber added to the plastics to give added strength. This can make recovery difficult.

### 2.8.2 Sources of Waste Plastics

Industrial waste (or primary waste) can often be obtained from the large plastics processing, manufacturing and packaging industries. Rejected or waste material usually has good characteristics for recycling and will be clean. Although the quantity of material available is sometimes small, the quantities tend to be growing as consumption, and therefore production, increases. Commercial waste is often available from workshops, craftsmen, shops, supermarkets and wholesalers. A lot of the plastics available from these sources will be PE, often contaminated. Agricultural waste can be obtained from farms and nursery gardens outside the urban areas. This is usually in the form of packaging (plastic containers or sheets) or construction materials (irrigation or

hosepipes). Municipal waste can be collected from residential areas (domestic or household waste), streets, parks, collection depots and waste dumps. In Asian cities this type of waste is common and can either be collected from the streets or can be collected from households by arrangement with the householders.

### 2.8.3 Processing of Reclaimed Plastics

#### 2.8.3.1 *Initial Upgrading*

Once the plastic has been collected, it will have to be cleaned and sorted. The techniques used will depend on the scale of the operation and the type of waste collected, but at the simplest level will involve hand washing and sorting of the plastics into the required groups. More sophisticated mechanical washers and solar drying can be used for larger operations. Sorting of plastics can be by polymer type (thermoset or thermoplastic for example), by product (bottles, plastic sheeting, etc.), by colour, etc.

#### 2.8.3.2 *Size Reduction Techniques*

Size reduction is required for several reasons; to reduce larger plastic waste to a size manageable for small machines, to make the material denser for storage and transportation, or to produce a product which is suitable for further processing. There are several techniques commonly used for size reduction of plastics.

#### 2.8.3.3 *Cutting*

This process is usually carried out for initial size reduction of large objects. It can be carried out with scissors, shears, saw, etc.

#### 2.8.3.4 *Shredding*

This is suitable for smaller pieces. A typical shredder has a series of rotating blades driven by an electric motor, some form of grid for size grading and a collection bin. Materials are fed into the shredder via a hopper which is sited above the blade rotor. The product of shredding is a pile of coarse irregularly shaped plastic flakes which can then be further processed.

#### 2.8.3.5 *Agglomeration*

Agglomeration is the process of pre-plasticising soft plastic by heating, rapid cooling to solidify the material and finally cutting into small pieces. This is usually carried out in a single machine. The product is coarse, irregular grain, often called crumbs.

#### 2.8.3.6 *Further Processing Techniques*

The process of extrusion is employed to homogenise the reclaimed polymer and produce a material that is subsequently easy to work. The reclaimed polymer pieces are fed into the extruder, are heated to induce plastic behaviour and then forced through a die (see the following section on manufacturing techniques) to form a plastic spaghetti which can then be cooled in a water bath before being pelletised. The pelletisation process is used to reduce the 'spaghetti' to pellets which can then be used for the manufacture of new products.

### 2.8.4 Manufacturing Techniques

#### 2.8.4.1 *Extrusion*

The extrusion process used for manufacturing new products is similar to that outlined above for the process preceding pelletisation, except that the product is usually in the form of a continuous 'tube' of plastic such as piping or hose.

The reclaimed plastic is forced along the heated tube by an archimedes screw and the plastic polymer is shaped around a die. The die is designed to give the required dimensions to the product and can be interchanged.

#### 2.8.4.2 *Injection Molding*

The first stage of this manufacturing process is identical to that of extrusion, but then the plastic polymer emerges through a nozzle into a split mould. The quantity of polymer being forced out is carefully controlled, usually by moving the screw forward in the heated barrel. A series of molds would be used to allow continual production while cooling takes place. This type of production technique is used to produce molded products such as plates, bowls, buckets, etc.



#### 2.8.4.3 *Blow Molding*

Again the spiral screw forces the plasticised polymer through a die. A short piece of tube or parison is then enclosed between a split die, which is the final shape of the product, and compressed air is used to expand the parison until it fills the mold and achieves its required shape. This manufacturing technique is used for manufacturing closed vessels such as bottles and other containers.

#### 2.8.4.4 *Film blowing*

Film blowing is a process used to manufacture such items as garbage bags. It is a technically more complex process than the others described in this brief and requires high quality raw material input. The process involves blowing compressed air into a thin tube of polymer to expand it to the point where it becomes a thin film tube. One end can then be sealed and the bag or sack is formed. Sheet plastics can also be manufactured using a variation of the process described.

#### 2.8.5 Products from Recycled Plastic

There is an almost limitless range of products that can be produced from plastics. However, the market for recycled plastic products is limited due to the inconsistency of the raw material. Many manufacturers will only incorporate small quantities of well-sorted recycled material in their products whereas others may use a much higher percentage of recycled polymers. Much depends on the quality required. In developing countries, where standards are often lower and raw materials very expensive, there is a wider scope for use of recycled plastic material. The range of products varies from building materials to shoes, kitchen utensils to office equipment, sewage pipe to beauty aids.

### 2.9 Previous Research

Mechanical recycling of 100% post-consumer plastic wastes into high quality products has been performed. (Ambrose et al., 2002: 309-318) The chemical and physical properties of these recycled materials have been compared with similar

products manufactured from virgin resins. The properties of a blow-molded bottle prepared from 100% post-consumer high-density polyethylene (HDPE) showed that this recycled polymer exceeded the materials specifications for virgin plastic designs. Similarly, a sample of thermoplastic polyolefin (TPO, 100% polypropylene), obtained entirely from shredder residue (SR) displayed sufficient material strength for future separation and reprocessing.

Post-consumer high density polyethylene (HDPE) was examined by a test procedure consisting of repeated cycles of alternating extrusion and subsequent accelerated thermo-oxidative ageing. (Bolizar et al., 2000: 317-319) The material studied was collected from a real waste stream of HDPE bottles. The effect of addition of a commercial re-stabilizer was also studied. The material was evaluated in terms of mechanical and chemical properties, such as elongation at break, tensile strength, melt flow rate, oxygen induction temperature and molar mass distributions. The results show that after simulated recycling the HDPE material still has considerable resistance against thermal degradation. Upon an additional period of accelerated ageing the stability of the material was still high. The presence of re-stabilizer, introduced during extrusion in the simulated recycling procedure, increased the resistance to subsequent thermo-oxidative ageing. However, significant cross-linking and/or molecular enlargement were found.

The recyclability of the two main polyolefins from municipal plastic waste, HDPE and PP, was evaluated. (Santos et al., 2002: 441-447) The HDPE/PP blend (90:10), which is the most commonly found weight proportion, was extruded three times at conventional ( $150\text{--}180^{\circ}\text{C}$ ) and high ( $210\text{--}250^{\circ}\text{C}$ ) reprocessing temperatures. The behavior of degradation was evaluated by infrared spectroscopy measurements (carbonyl index), melt flow index (MFI), capillary rheometry and differential scanning calorimetry (oxidation induction time, OIT). Different antioxidant additive concentrations were prepared according to the steps at which a considerable level of degradation was observed, including an evaluation of the best benefit/cost ratio of the studied additive formulations.

Determining retained properties and durability is among the most important tasks when evaluating the possibility of mechanical recycling of plastic waste. (Yaramadi et al., 2001: 93-99) In this investigation, profiles made of rigid PVC have been studied after various numbers of repeated extrusions to gain knowledge about the changes of properties and durability after conventional processing. New indoor profiles of PVC were re-extruded, from one to five times without adding new additives. The material was characterized after each extrusion using measurements of color, degree of gelation, stress-strain at break and UV-VIS-NIR spectroscopy. The durability of the material was evaluated by accelerated ageing in ventilated heat ovens with low laminar airflow, at various temperatures. Changes in elongation at break, color and chemical characteristics, depending on degradation, were measured and compared for the material after each extraction and various periods of ageing time. The material showed an improvement of mechanical properties after the second extrusion. This is explained by an increase in the degree of gelation of the PVC material. The main color change due to repeated extrusion was yellowing. In accelerated heat ageing, the main color change was towards red and a change in grayness as a result of thermal dehydrochlorination. The activation energies of the degradation were also determined for the material after each re-extrusion and were found to decrease with an increasing number of extrusions. The estimated lifetime for indoor use at room temperature for the material after five extrusions was one-third of the lifetime of the material extruded only once. Despite this finding, a long lifetime can be expected even for the material subjected to five consecutive extrusions, making the material suitable for mechanical recycling.

Many of the physical, chemical and utility properties of polymer materials can be altered by means of high energy radiation such as gamma-rays, neutrons and electron beams. (Suarez et al., 2002: 143-151) The exposure to gamma radiation of a bulk virgin low density polyethylene (LDPE) was carried out at various doses up to 2000 kGy. The study of the irradiation effects on the material properties has been making by different methods in an integrated way. The experimental data indicate that the gel content, the hardness and the yellowing increase with gamma radiation dose and that the LDPE

gamma irradiation process involves cross-linking at lower doses and chain scission at higher doses. The final results show the reliability of gamma radiation as a practical method for the control of long-term properties.

The photodegradation mechanism of polymers highly depends on the type and concentration of chromophores present. (Gijsman et al., 1999: 433-441) This influence is studied by making a comparison between the UV-degradation of PE, PP, PA6 and PBT and the thermooxidative degradation of PP at a comparable temperature. The degradation processes are followed by determining the oxygen uptake, CO, CO<sub>2</sub> and peroxide formation. During UV-degradation of PP, PE, PA6 and PBT the oxygen uptake is linear in time without an induction period. The oxidation rate of PP is higher than that of PBT, which is slightly higher than the oxidation rate of PA6, while that of PE is the lowest. The determined amount of peroxides depends on the ageing time. For the UV-degradation this does not lead to the expected increase of the oxidation rate, as is the case with thermo-oxidation of PP. Only a limited proportion of the peroxides formed during the UV-degradation decompose into radicals. The oxidation rate is mainly determined by other radical forming reactions. In the case of PE and PP this is probably initiation by polymer-oxygen Charge Transfer Complexes (CTCs) and for PA6 and PBT direct photolysis of the amide or the ester linkage, respectively. Thickness degradation profiles show that the UV- degradation processes of PP and PBT are heterogeneous. For PP this is due to oxygen diffusion limitation, while in the case of PBT it is the result of absorption of the UV-light.

Quantitative FTIR-emission spectroscopy was applied to investigate the real-time thermal oxidation of polyolefin samples and shown to be a useful method for studying polymer degradation. (George et al., 1995: 199-210) The high sensitivity of the technique was demonstrated by studying the oxidation of individual pressed polypropylene (PP) and high density polyethylene (HDPE) reactor powder particles and microtome cuttings of cross-linked polyethylene (XLPE). A detailed analysis of the growth in carbonyl bands during the degradation showed no changes in the product distribution with time. Secondary oxidation products, such as  $\gamma$ -lactones in the case of

polypropylene, were observed from the onset of the degradation, which is consistent with a model of oxidation occurring in localized zones with high reactivities. Differences in the oxidation sensitivity of these materials were identified and attributed to variations in the stability of the PP particles, catalyst residues in the HDPE and the degree and method of cross-linking of the XLPE.



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## Chapter 3

### EXPERIMENTAL

In this chapter, experimental details are explained. Various grades of commercial polyolefin resins, namely, polypropylene (PP) and polyethylene (PE), were used in this research. In order to simulate recycling situation, each resin was repeatedly extruded and injected for 10 times. After each cycle, part of the product was collected and tested for its properties. Melt flow index (MFI) was used to study the structural changes, especially those affected to molecular weight. MFI is also a crucial data for processing. The Fourier transform infrared spectroscopy (FTIR) technique was used to determine the changes in molecular structure as well. The collected plastics were also processed into test specimens for determining their tensile properties. Yellowing phenomena was explored using the yellowness index and was confirmed by FTIR data. In short, the experimental procedure can be illustrated as in Figure 3.1 and Figure 3.6. Materials and methods are explained in the following section.



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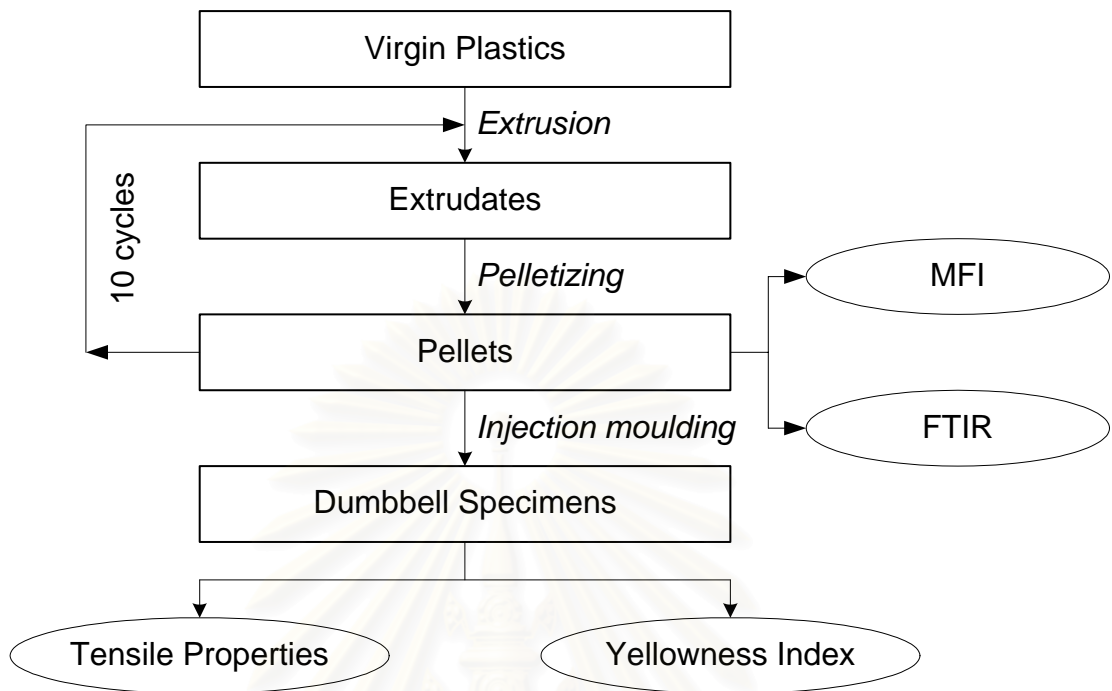


Figure 3.1 Experimental procedure for extrusion process

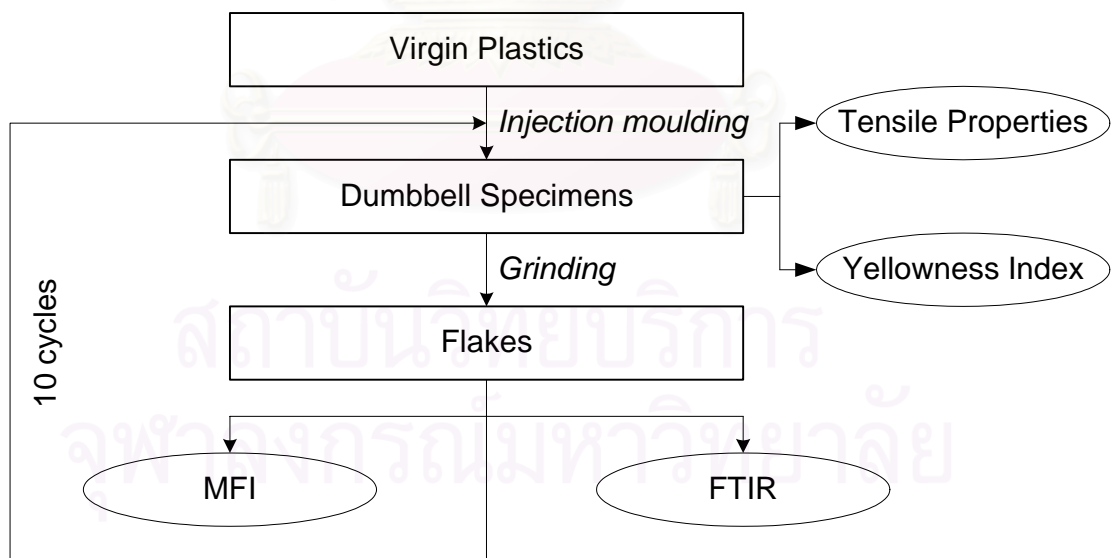


Figure 3.2 Experimental procedure for injection process

### 3.1 Materials

Polypropylene (PP) was supplied by CCC Chemical Commerce Co.,Ltd., Thailand. The extrusion grade, P400S, and the injection grade, P702J, were selected. Some of their properties were shown in Table 3.1 and Table 3.2.

Table 3.1 Properties of PP (extrusion grade) used in this experiment

Physical properties	Unit	Testing method	Value
Melt Flow Rate	g / 10 min	ASTM D 1238	3.5
Density	g / cm <sup>3</sup>	ASTM D 1505	0.910
Tensile strength at yield	kg / cm <sup>2</sup>	ASTM D 638	380
Tensile strength at break	kg / cm <sup>2</sup>	ASTM D 638	350
Elongation at break	%	ASTM D 638	500
Flexural modulus	kg / cm <sup>2</sup>	ASTM D 790	16,000
Vicat Softening Point	°C	ASTM D 1525	155
Heat Deflection Temperature at 4.6 kg/cm <sup>2</sup>	°C	ASTM D 648	110

Table 3.2 Properties of PP (injection grade) used in this experiment

Physical properties	Unit	Testing method	Value
Melt Flow Rate	g / 10 min	ASTM D 1238	12.0
Density	g / cm <sup>3</sup>	ASTM D 1505	0.910
Tensile strength at yield	kg / cm <sup>2</sup>	ASTM D 638	420
Tensile strength at break	kg / cm <sup>2</sup>	ASTM D 638	380
Elongation at break	%	ASTM D 638	150
Flexural modulus	kg / cm <sup>2</sup>	ASTM D 790	17,000
Vicat Softening Point	°C	ASTM D 1525	155
Heat Deflection Temperature at 4.6 kg/cm <sup>2</sup>	°C	ASTM D 648	115



Low density polyethylene (LDPE) was supplied by CCC Chemical Commerce Co.,Ltd., Thailand. The extrusion grade, LD1905F, and the injection grade, LD1450J, were selected. Some of their properties were shown in Table 3.3.

Table 3.3 Properties of LDPE (extrusion grade) used in this experiment

Physical properties	Unit	Testing method	Value
Melt Flow Rate	g / 10 min	ASTM D 1238	5.0
Density	g / cm <sup>3</sup>	ASTM D 1505	0.919
Tensile strength at break	kg / cm <sup>2</sup>	ASTM D 638	210
Elongation at break	%	ASTM D 638	320
Flexural modulus	kg / cm <sup>2</sup>	ASTM D 790	2,100
Vicat Softening Point	°C	ASTM D 1525	90
Heat Deflection Temperature at 4.6 kg/cm <sup>2</sup>	°C	ASTM D 648	110

High density polyethylene (HDPE) was supplied by CCC Chemical Commerce Co.,Ltd., Thailand. The extrusion grade, H5480S, and the injection grade, H6007, were selected. Some of their properties, providing by the company, were shown in Table 3.4.

Table 3.4 Properties of HDPE (extrusion grade) used in this experiment

Physical properties	Unit	Testing method	Value
Melt Flow Rate	g / 10 min	ASTM D 1238	0.8
Density	g / cm <sup>3</sup>	ASTM D 1505	0.954
Tensile strength at yield	kg / cm <sup>2</sup>	ASTM D 638	260
Tensile strength at break	kg / cm <sup>2</sup>	ASTM D 638	390
Elongation at break	%	ASTM D 638	>900
Flexural modulus	kg / cm <sup>2</sup>	ASTM D 790	10,000
Vicat Softening Point	°C	ASTM D 1525	123

Table 3.5 Properties of HDPE (injection grade) used in this experiment

Physical properties	Unit	Testing method	Value
Melt Flow Rate	g / 10 min	ASTM D 1238	7.5
Density	g / cm <sup>3</sup>	ASTM D 1505	0.967
Tensile strength at yield	kg / cm <sup>2</sup>	ASTM D 638	310
Tensile strength at break	kg / cm <sup>2</sup>	ASTM D 638	220
Elongation at break	%	ASTM D 638	>650
Flexural modulus	kg / cm <sup>2</sup>	ASTM D 790	13,500
Vicat Softening Point	°C	ASTM D 1525	127

## 3.2 Sample Preparations

### 3.2.1 Extrusion Process

Extrusion-grade PP, LDPE and HDPE were repeatedly extruded in a single screw extruder (Powtran Invada 9308) as shown in Figure 3.3 using the extrusion conditions listed in Table 3.6.



Figure 3.3 Single screw extruder (Powtran Invada 9308)

Table 3.6 Extrusion conditions

Polyolefins	Temperature (°C)	Screw speed (rpm)
PP	230	15
LDPE	130	15
HDPE	280	15

The extrudates were cut into pellets using a pelletizer (Thermoprism No.4541).



Figure 3.4 Pelletizer (Thermoprism)

### 3.2.2 Injection Process

Injection grade PP and HDPE were repeatedly injected in an injection moulding machine (Cosmo) as shown in Figure 3.5.

Table 3.7 indicates the injection conditions used in this experiment.



Figure 3.5 Injection molding machine (Cosmo)

Table 3.7 Injection conditions

Polyolefins	Temperature (°C)	Screw speed (rpm)
PP	230 - 280	15
HDPE	200 - 280	15

The injected specimens could be separated into several test specimen forms as shown in Figure 3.6.

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Figure 3.6 Injected sample

Some samples were ground into granules using a plastic grinding mill as shown in Figure 3.7.



Figure 3.7 Plastic grinding mill

### 3.3 Characterization and Testing

#### 3.3.1 Melt Flow Index

The rheological property of PP, LDPE and HDPE was studied by a melt flow index tester as shown in Figure 3.8. The melt flow index (MFI) was evaluated at 230°C for PP, 190°C for LDPE and 280°C for HDPE with 2.16 kg weight following ASTM D1238-00. At least five specimens were tested to obtain the average value of each plastic grade with standard variation less than 5%. This test measure the rate of extrusion of molten resins through a die of specified length and diameter under conditions of temperature, load, and piston position in the barrel as the timed measurement is being made. The apparatus shall be a dead-weight piston plastometer. The test specimen may be in granule form or pellet form that can be introduced into the bore of the cylinder. Selecting conditions of temperature and load The temperature of the cylinder with the piston and die in place shall have been at the test temperature for at least 15 min before a test is begun. Remove the piston and place it on an insulated surface. Charge the cylinder within 1 min with a weighed portion of the sample and start timing for a 6 to 8 min preheat.



Figure 3.8 Melt flow index tester (Kayeness 7053)

### 3.3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra of the samples were obtained using Nicolet Impact FT-IR spectrometer scans at resolutions of  $4000 - 400 \text{ cm}^{-1}$  was observed. The spectrum of each sample was recorded in the film state. Films were prepared by placing plastic pellets or granules between two glass slides and bringing to heat. The plastics were melted by using the weight putting on top of the glass slide. Films were formed when the plastics were cooled down. The absorbance was obtained accordingly.



Figure 3.9 Fourier Transform Infrared Spectroscopy (Nicolet Impact 400D)

### 3.3.3 Tensile Properties

Tensile testing was performed according to the ASTM D638-00 on a universal testing machine (LLOYD LR 100K). The standard dumbbell specimens were prepared with dimensions described in

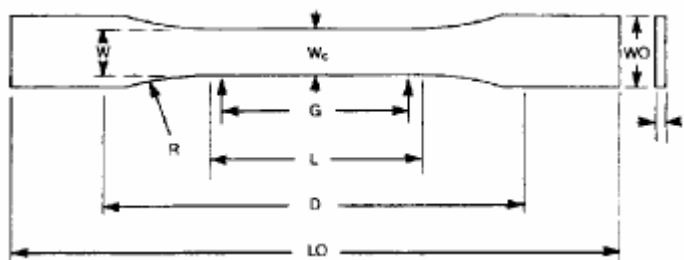


Figure 3.10 Tensile test specimen as corresponding to size specified in Table 3.8

Table 3.8. The grip was used. During the test, the specimens are elongated at 500 mm/min with an initial gauge length of 50 mm. The Nexygen software was used to process the acquired data. The 'pull to break' set up with 100 KN of load cell was used in this research. The number of specimens were selected so that the coefficient variation was less than 10%.

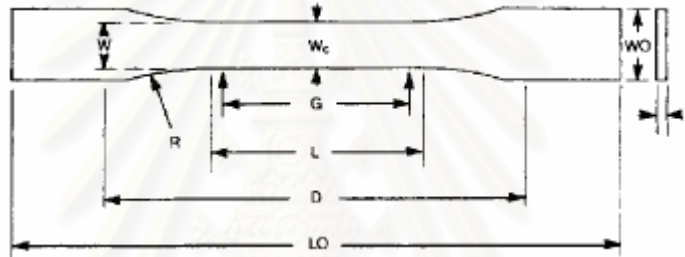


Figure 3.10 Tensile test specimen as corresponding to size specified in Table 3.8

Table 3.8 Dimensions of tensile test specimen

Dimensions (see Figure 3.10)	ASTM Type I
W- Width of narrow section	13 mm.
L- Length of narrow section	57 mm.
WO- Width overall, min	19 mm.
LO- Length overall, min	165 mm.
G- gage length	50 mm.
D-distance between grip	115 mm.
R-Radius of fillet	76 mm.





Figure 3.11 Universal testing machine (Lloyd LR100K)

#### 3.3.4 Yellowness Index

In order to observe yellowing phenomena in reprocessed plastics, the yellowness index was measured using a spectrophotometer (Macbeth ColorEye 7000). ASTM D 1925-00 was followed.



Figure 3.12 Spectrophotometer (Macbeth ColorEye 7000)

## Chapter 4

### RESULTS AND DISCUSSION

The experimental results are reported in this chapter. Changes in molecular structures as indicated by the melt flow index (MFI), tensile properties and yellowing phenomenon as related to the amount of reprocessing cycles are discussed.

#### 4.1 Polypropylene (PP)

##### 4.1.1 Melt Flow Index

In this research, the melt flow index (MFI) was used to observe the changes in molecular structures. It is widely known that melt flow index is a good predictor of molecular weight of plastics. As molecular weight of a plastic increases, the melt flow index decreases and vice versa.

Figure 4.1 shows the MFI of polypropylene passing through different re-extrusion cycles. Evidently, the MFI was continuously increased as the number of re-extruding cycles increased. The increasing MFI was resulted from the decreasing in molecular weight and the molecular weight reduction was, in turn, resulted from the chain scission due to thermal degradation and shear force receiving from passing each processing cycle.

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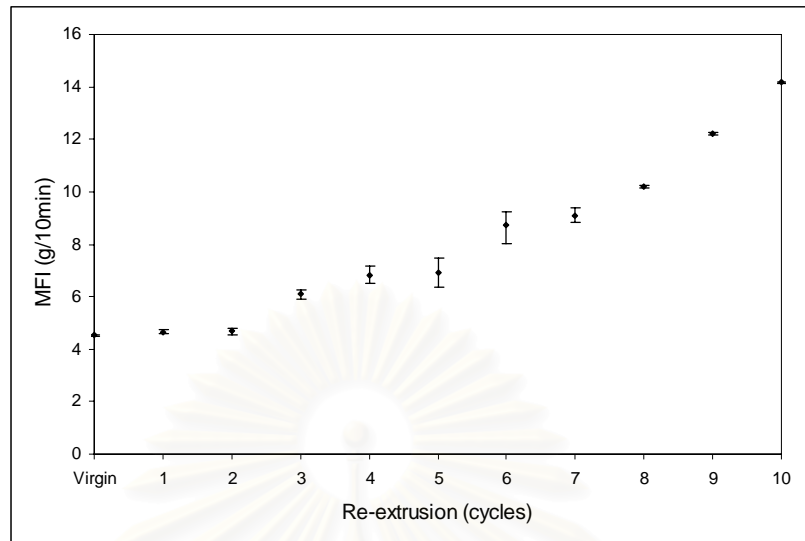


Figure 4.1 MFI of re-extruded PP

Figure 4.2 shows the MFI of injected PP passing through re-injection cycles. It can be concluded that, when plastics were exposed to heat and stress, the MFI was continuously increased as the number of re-injection cycles increased. The increasing MFI was resulted from the decreasing in molecular weight and the molecular weight reduction was, in turn, resulted from the chain scission of PP due to heat degradation and shear force that occurred in the process. This is in the same trend as in the re-extruded PP.

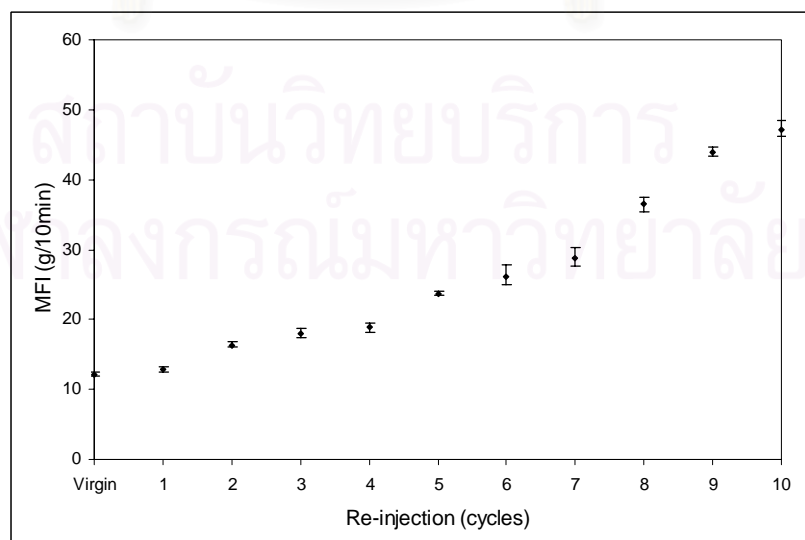


Figure 4.2 MFI of re-injected PP

In order to confirm our assumption, samples were collected and prepared to be investigated by FTIR. From FTIR analysis, the ratio between absorbance at  $1370\text{-}1390\text{ cm}^{-1}$  indicating  $\text{CH}_3$  symmetrical deformation and at  $1430\text{-}1470\text{ cm}^{-1}$  indicating  $\text{CH}_2$  and  $\text{CH}_3$  deformation was calculated. This ratio is called the methyl index. Figure 4.3 shows the methyl indices of virgin PP, re-extruded PP at the 5<sup>th</sup> and the 10<sup>th</sup> cycles. Being the end chain functional groups, the increase in the methyl index implied that molecular chains were shorter due to chain scission.

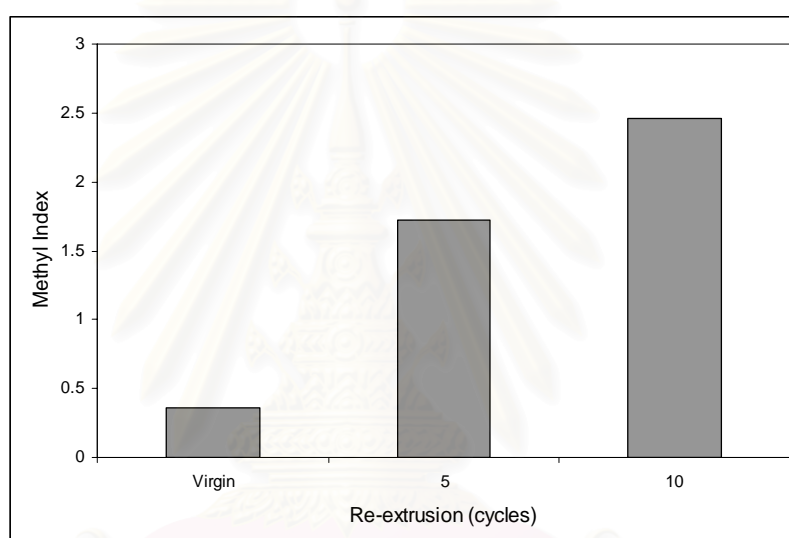


Figure 4.3 Methyl indices of re-extruded PP

Figure 4.4 shows the methyl indices of virgin PP and re-injected PP at the 5<sup>th</sup> and the 10<sup>th</sup> cycles. It was found that the methyl indices slightly increased, indicating that the amount of  $\text{CH}_3$  groups increased. This is in agreement with the changes of MFI.

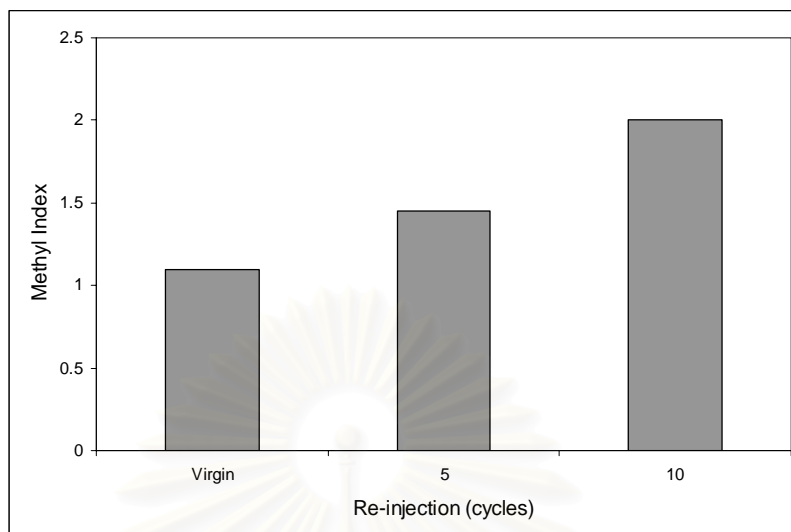


Figure 4.4 Methyl indices of re-injected PP

#### 4.1.2 Tensile Properties

The effects of the reprocessing on tensile properties of PP and PE were studied by a universal testing machine according to ASTM D638-00. From the test results, three properties, that are tensile modulus, tensile strength and elongation at break, were achieved. The tensile strength is defined as the maximum stress. In this research, the tensile modulus is defined as the slope of the tangent to the stress-strain curve at 10% strain. The elongation at break is the maximum strain shown by the test sample at the point of sample breakage. The three properties are shown in Figure 4.5 to Figure 4.10. It should be known that the tensile stress-strain relationship of a polymer depends on both the temperature and the cross head speed. Hence, the temperature was ambient and the cross head speed was used at 500 mm/min, corresponding to the highest speed indicated in ASTM D638-00.

Figure 4.5 shows the tensile strength of extruded PP passing through different re-extrusion cycles. Evidently, the tensile strength of re-extruded PP tended to reduce as the number of re-extrusion increased. The slowly decreasing or almost constant tensile strength was resulted from the reduction of molecular weight caused by thermal degradation. These results were related to the increment of MFI discussed earlier.

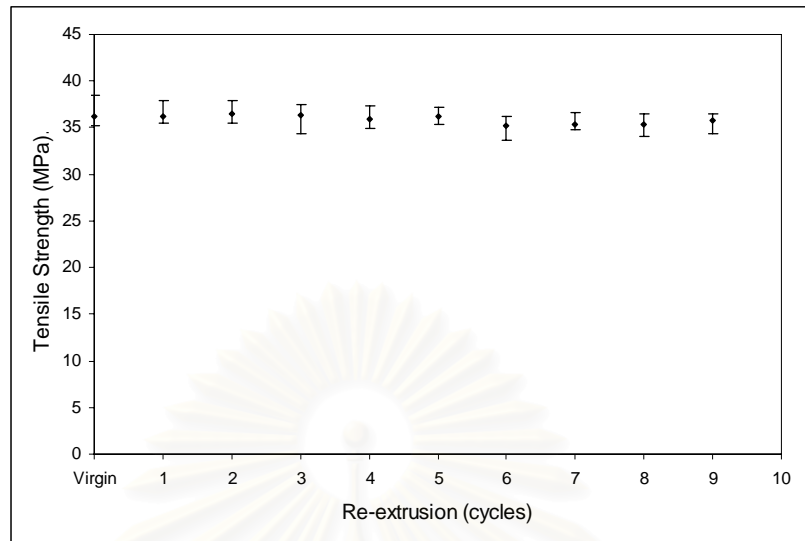


Figure 4.5 Tensile strength of re-extruded PP

Figure 4.6 shows the tensile strength of injected PP passing through different re-injected cycles. Evidently, the tensile strength of re-injected PP was almost unchanged as the number of re-injection cycles increased.

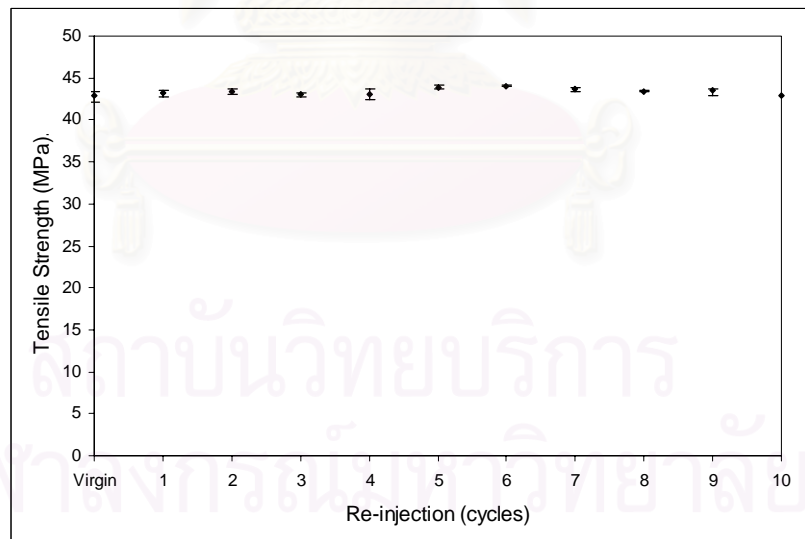


Figure 4.6 Tensile strength of re-injected PP

The elongation at break was constant as shown in Figure 4.7.

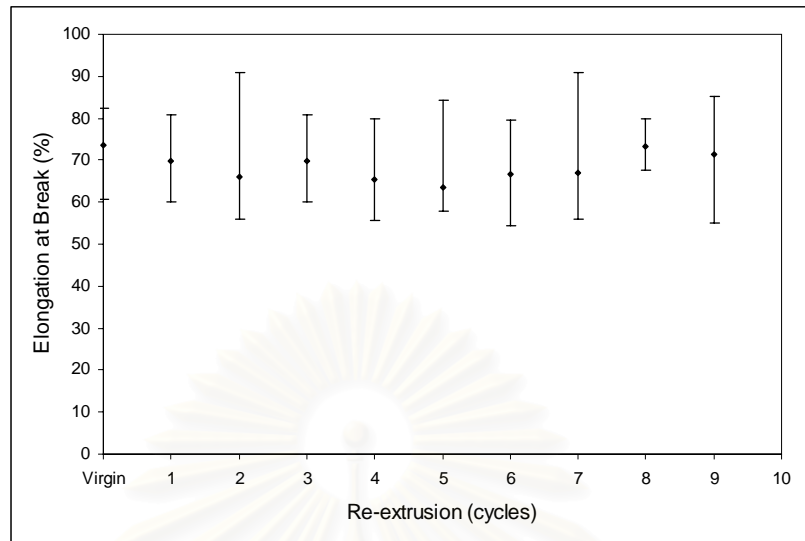


Figure 4.7 Elongation at break of re-extruded PP

Figure 4.8 shows the elongation at break of re-injected PP. It decreased slowly as the number of reprocessing cycles increased.

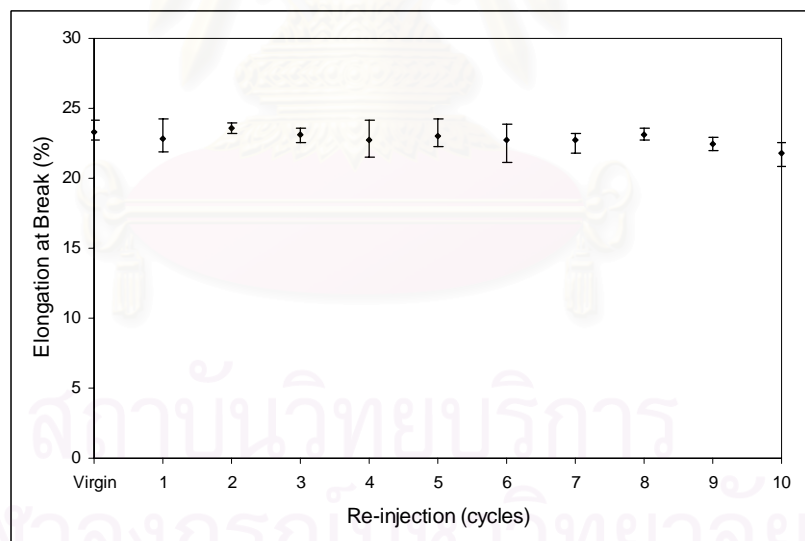


Figure 4.8 Elongation at break of re-injected PP

Figure 4.9 shows the tensile modulus of re-extruded PP that associated to the molecular weight. The decline of modulus was in the same trend as in tensile strength.

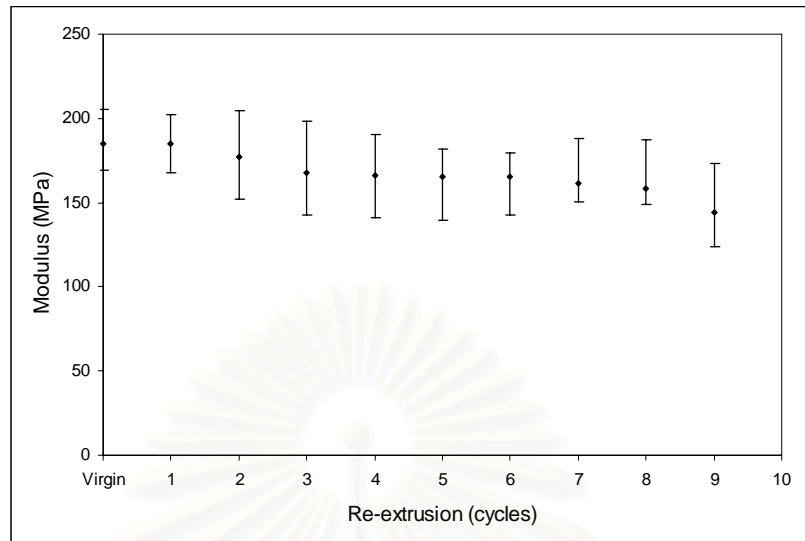


Figure 4.9 Tensile modulus of re-extruded PP

Figure 4.10 shows the modulus of re-injected PP that was decreased slowly depending on the reprocessing cycles.

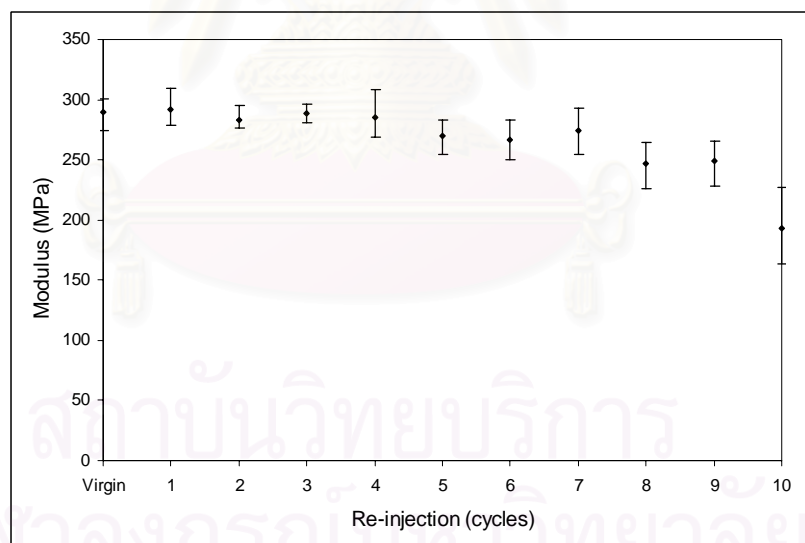


Figure 4.10 Tensile modulus of re-injected PP

#### 4.1.3 Yellowing Phenomena

Plastics tend to change its color after re-extrusion due to the formation of chromophoric groups, e.g. carbonyl groups or vinyl groups. The spectrophotometer was



used for investigating the color changes in terms of yellowness. The yellowness is increased when the number of re-processing increased.

Figure 4.11 shows the values of yellowness index of re-extruded PP. The yellowness are related to the quantity of chromophoric groups that occurs during thermal degradation. Consequently, if plastics were subjected to repeated heat and stress, yellowing would occur.

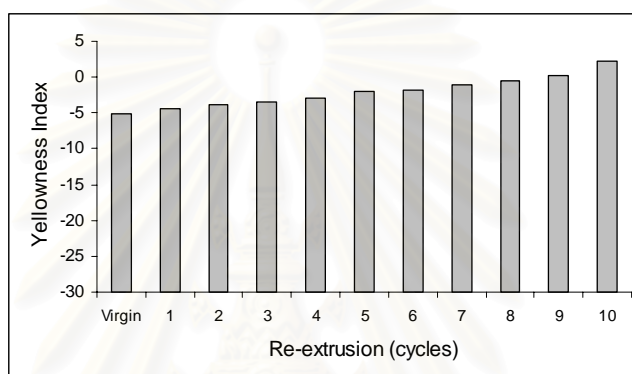


Figure 4.11 Yellowness of re-extruded PP

From the FT-IR analysis, the ratio between absorbance at  $985-995\text{ cm}^{-1}$  indicating vinyl and at  $1430-1470\text{ cm}^{-1}$  indicating  $\text{CH}_2$  and  $\text{CH}_3$  deformation was calculated. This ratio is called the vinyl index.

Figure 4.12 pointed out that there were changes in the amount of vinyl groups when plastics were undergone re-extrusion. This is inconsistent with the increasing value of yellowness.

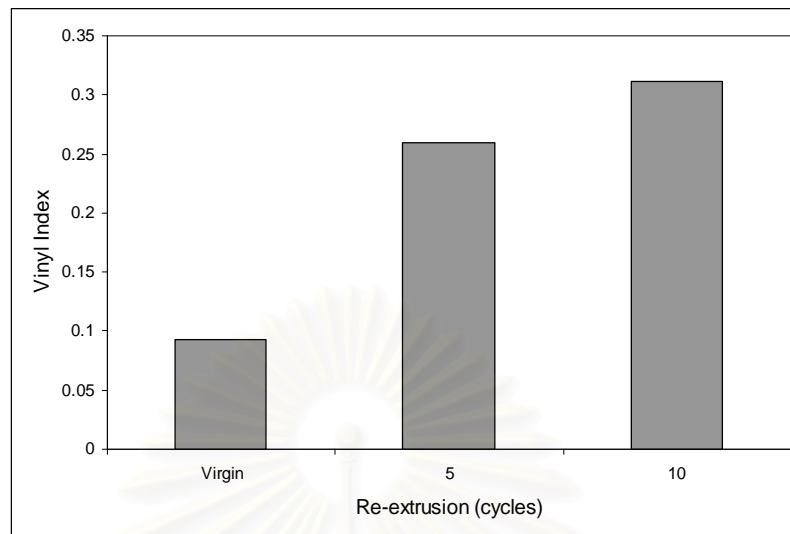


Figure 4.12 Vinyl indices of re-extruded PP

Figure 4.13 shows the value of yellowness from re-injection process. The yellowness are related to the quantity of vinyl groups that occurs during thermal degradation. Yellowing in plastics occurs as chromophoric groups are increased. If plastics were undergone repeated heating, yellowing would occur. In polyolefins, these are carbon double bonds, especially, vinyl, vinylene and vinylidene groups.

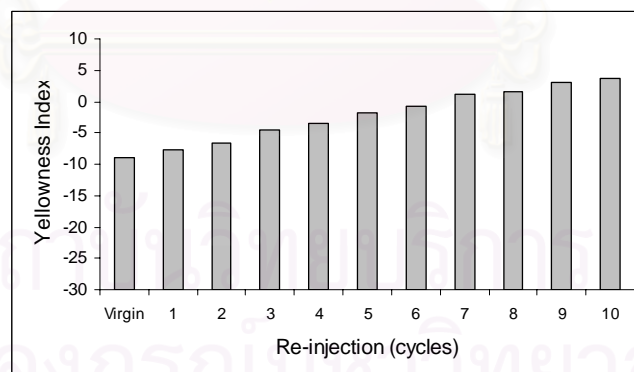


Figure 4.13 Yellowness of re-injected PP

Figure 4.14 pointed out that there were changes in the amount of vinyl groups when plastics were undergone the re-injected. It was expected that the vinyl index should be increased. However it was pointed out in Figure 4.14 that the vinyl index was decreased. This was probably due to the fact that the amount of  $\text{CH}_2$  deformation was increased in the much larger extent than the increasing of the amount of vinyl group,

resulting in the decreasing of vinyl index. The increase in  $\text{CH}_2$  groups was previously shown in Figure 4.30.

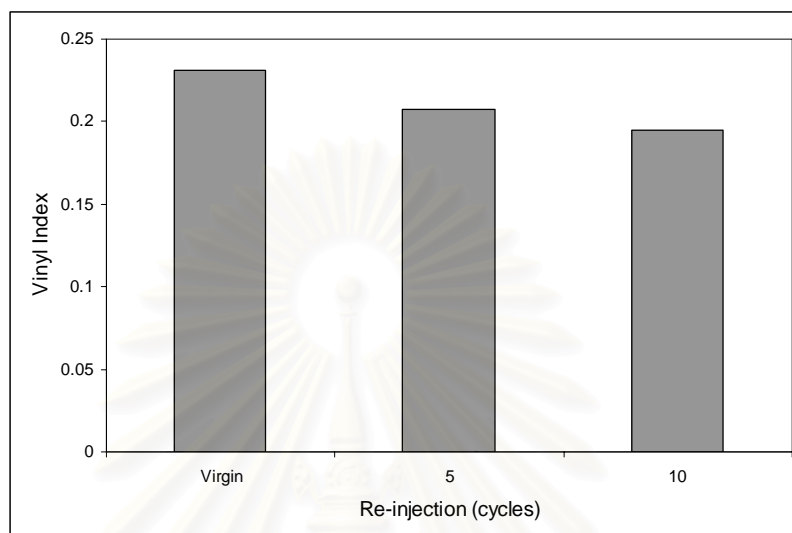


Figure 4.14 Vinyl indices of re-injected PP

## 4.2 High Density Polyethylene (HDPE)

### 4.2.1 Melt Flow Index

In the case of HDPE, as shown in Figure 4.15, the MFI of HDPE in the 1<sup>st</sup> cycle to the 6<sup>th</sup> cycle was largely decreased as the number of re-processing was increased. The cause of MFI reduction is that the cross-linking is the dominant regime in the overall degradation. The MFI of HDPE in the 7<sup>th</sup> cycle to the 8<sup>th</sup> cycle was constant. Then, the increasing of MFI was seen again in the 8<sup>th</sup> cycle to the 10<sup>th</sup> cycle. The MFI increment is the result of chain scission which overcame cross-linking in the degradation.

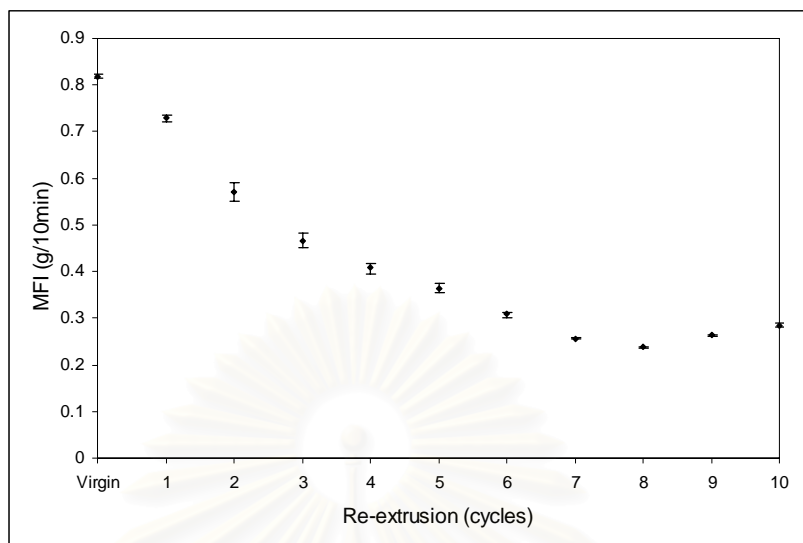


Figure 4.15 MFI of re-extruded HDPE

Figure 4.16 shows the melt flow index of injected HDPE passing through different re-injection cycles. It can be concluded that, when plastics were undergone the heating, the MFI was continuously decreased as the number of reprocessing cycles increased. The decreasing MFI of HDPE was resulted from higher molecular weight. It was assumed that crosslinking is the dominating regime. At the 9<sup>th</sup> and the 10<sup>th</sup> cycles, the MFI seem to be constant indicating competitive rate of chain scission.

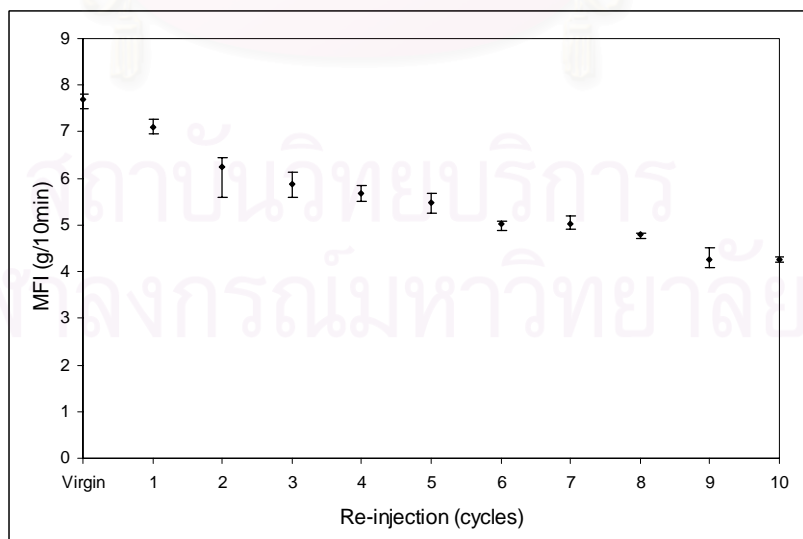


Figure 4.16 MFI of re-injected HDPE

From FTIR analysis, Figure 4.17 shows the methyl indices of virgin HDPE, re-extruded HDPE at the 5<sup>th</sup> and the 10<sup>th</sup> cycles. Being the end chain functional group, the decrease at the 5<sup>th</sup> cycle in the methyl index implied that the molecular chains contain less methyl groups. Thus, crosslinking is assumed to be dominating reaction. At the 10<sup>th</sup> cycle, the methyl index indicated that either methyl groups were reduced or -CH<sub>2</sub>- groups increased. It can be implied that molecular chains were shorter due to chain scission.

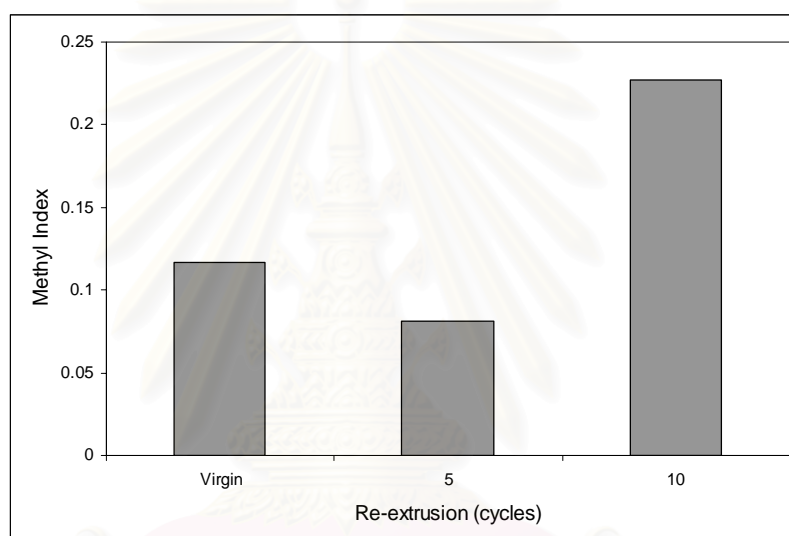


Figure 4.17 Methyl indices of re-extruded HDPE

From FTIR analysis, Figure 4.18 shows the methyl index of virgin HDPE, repeatedly injection HDPE at 5<sup>th</sup> and at 10<sup>th</sup> cycles. Being the end chain functional group, the decreased at the 5<sup>th</sup> cycles in the value of the methyl index implied that molecular chains crosslink and the increasing at ten cycles in the value of methyl index implied that molecular chains were shorter due to chain scission.

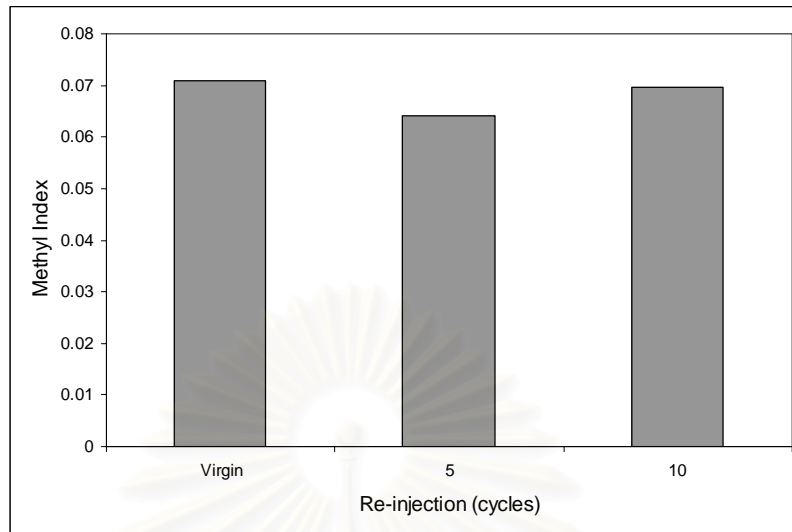


Figure 4.18 Methyl indices of re-injected HDPE

#### 4.2.2 Tensile Properties

Figure 4.19 shows the tensile strength of extruded HDPE passing through different re-extrusion cycles. Evidently, the tensile strength of re-extruded HDPE was increased. When HDPE was subjected to heat and stress, it will degrade. During degradation, chain scission and cross-linking are both occurred. The result indicated that cross-linking is the dominant reaction during the degradation of HDPE which is in agreement as described in the previous section.

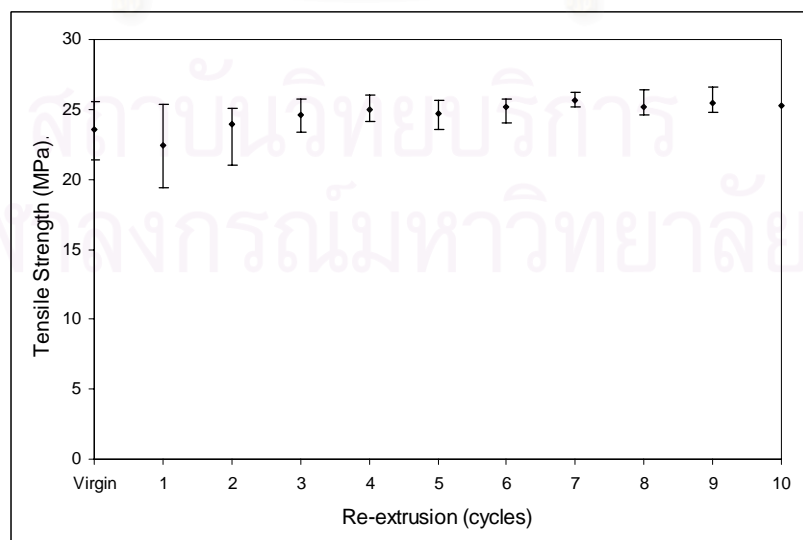


Figure 4.19 Tensile strength of re-extruded HDPE

Figure 4.20 shows the tensile strength of injected HDPE passing through different re-processing cycles. Evidently, the tensile strength of re-injected HDPE was constant as the number of re-injection increased.

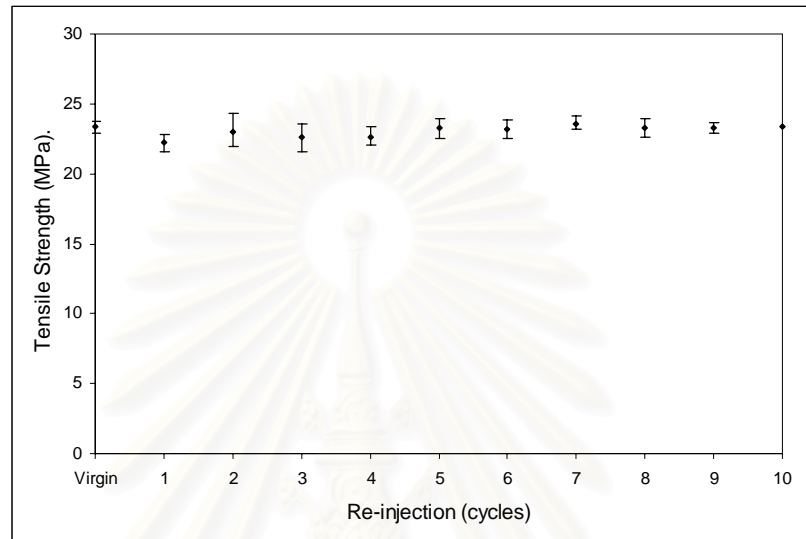


Figure 4.20 Tensile strength of re-injected HDPE

The elongation at break of re-extruded HDPE was decreased due to the fact that the specimens were more rigid due to cross-linking structure, as shown in Figure 4.21.

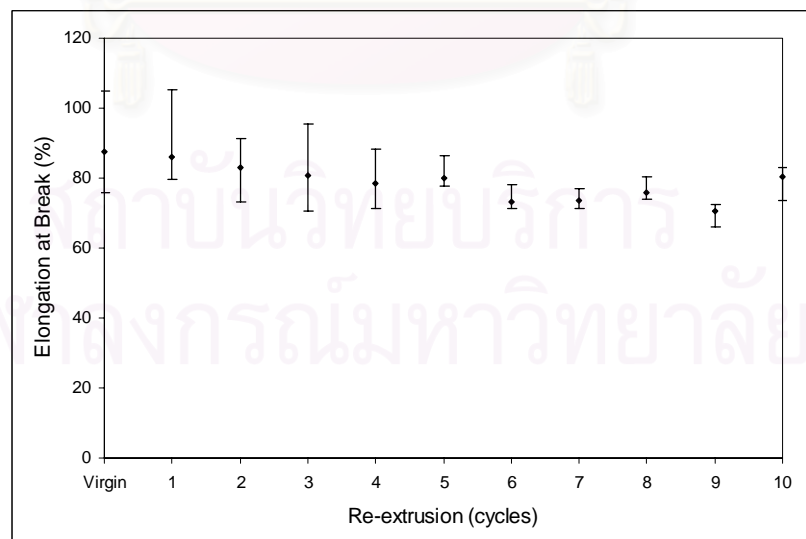


Figure 4.21 Elongation at break of re-extruded HDPE

Figure 4.22 shows the elongation at break which was decreased in the 1<sup>st</sup> cycle due to chain cross-linking. However, at the subsequent cycles, the elongation at break was increased since chain scission occurred in the advancing rate comparing with cross-linking. The elongation at break from the 8<sup>th</sup> to the 10<sup>th</sup> cycles was decreased slowly as the cross-linking rate was increased.

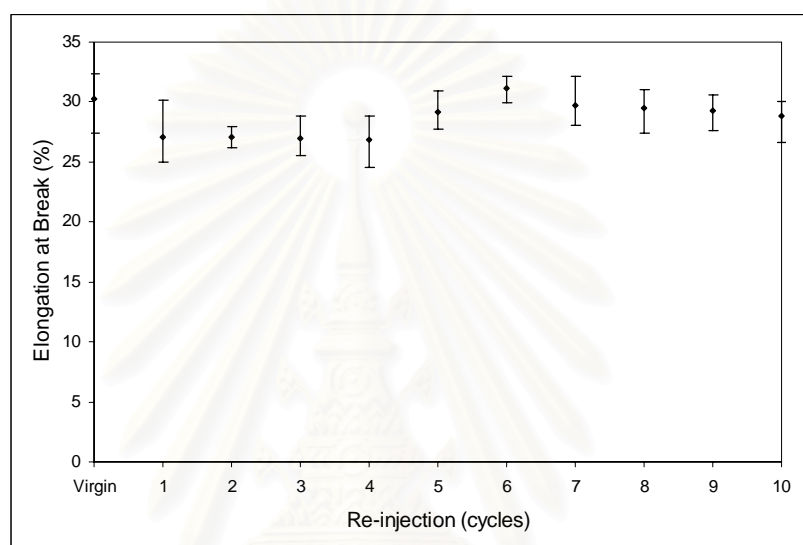


Figure 4.22 Elongation at break of re-injected HDPE

Figure 4.23 shows the modulus of re-extruded HDPE that tended to increase due to the increase of molecular weight. The increment of molecular weight is because cross-linking is dominantly occurred during thermal degradation.

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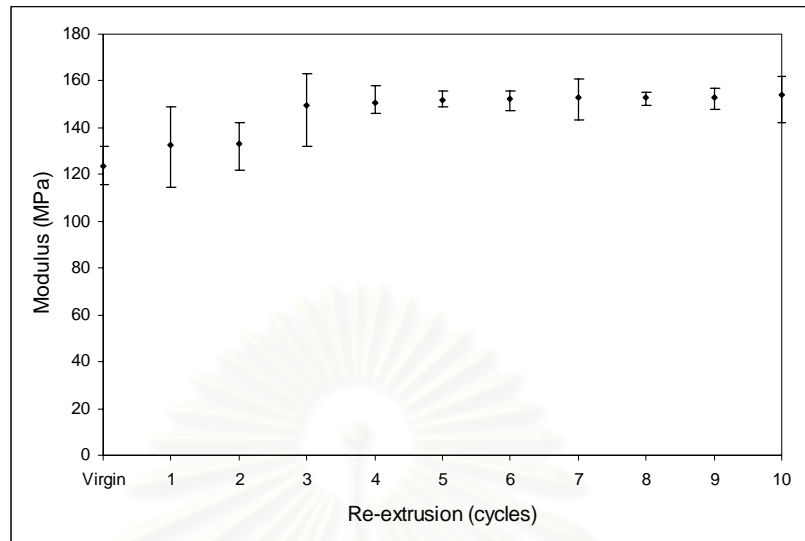


Figure 4.23 Tensile modulus of re-extruded HDPE

Figure 4.24 shows the modulus of re-injected of HDPE which was in the same trend as in the elongation at break result.

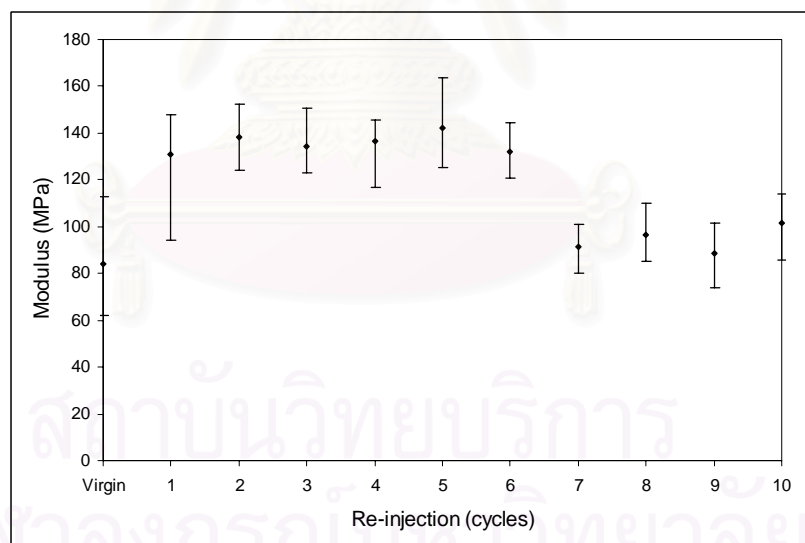


Figure 4.24 Tensile modulus of re-injected HDPE

#### 4.2.3 Yellowing Phenomena

Figure 4.25 shows the yellowness of HDPE under reprocessing cycles. The increasing of yellowness was caused by the presence of chromophoric groups, e.g. vinyl, vinylene and vinylidene groups in the polymer chains. The FT-IR can be used to

indicate changes in vinyl groups that related on the yellowing of plastic. The result from FT-IR shows in Figure 4.28. The vinyl index is corresponding with the yellowness.

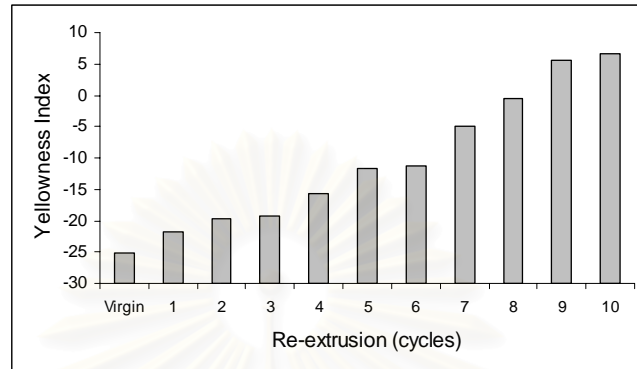


Figure 4.25 Yellowness of re-extruded HDPE

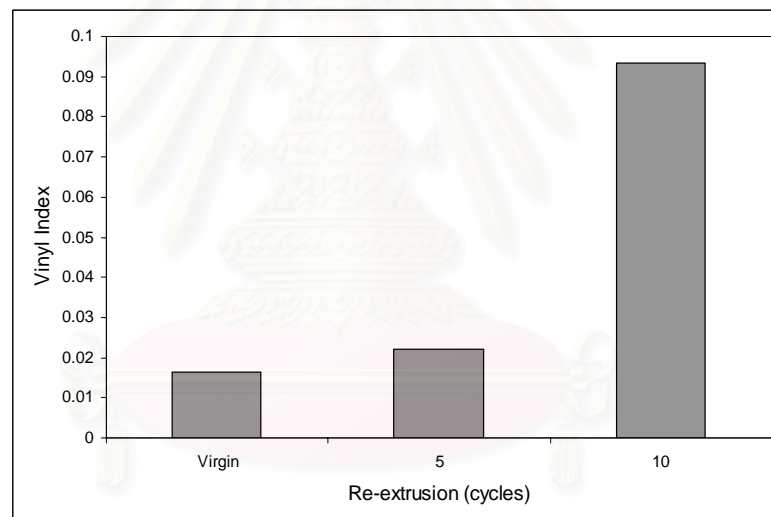


Figure 4.26 Vinyl indices of re-extruded HDPE

Figure 4.27 shows the yellowness of HDPE that undergone the re-injection cycles. The yellowness was increased when the amount of reprocessing cycles increased. The increment of yellowness were caused by the presence of chromophoric groups in the polymer chains.

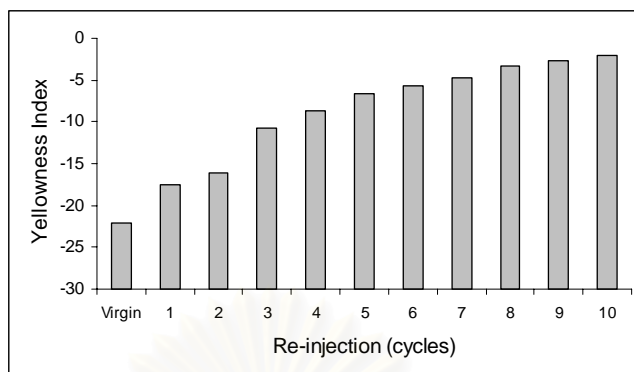


Figure 4.27 Yellowness of re-injected HDPE

The result from FT-IR which shows in Figure 4.28 can be used to imply the changes in vinyl groups. As the number of reprocessing increased, the vinyl index was increased.

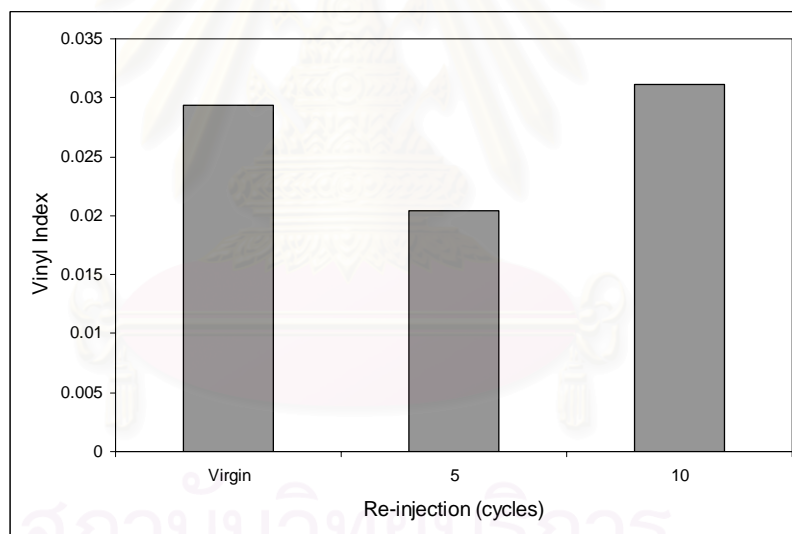


Figure 4.28 Vinyl indices of re-injected HDPE

### 4.3 Low Density Polyethylene (LDPE)

#### 4.3.1 Melt Flow Index

In the case of LDPE as shown in Figure 4.29, the MFI was almost constant.

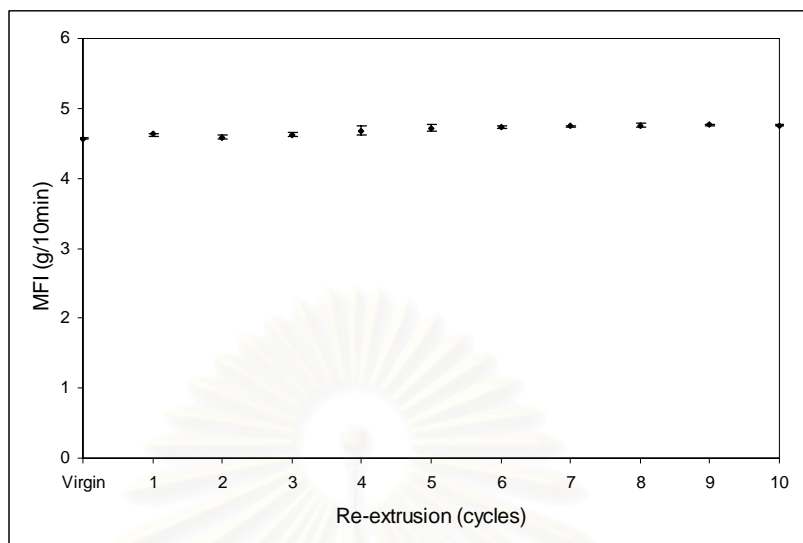


Figure 4.29 MFI of re-extruded LDPE

Figure 4.30 shows the methyl indices of virgin LDPE and re-extruded LDPE at the 5<sup>th</sup> and the 10<sup>th</sup> cycles. It was found that the methyl index was slightly reduced, indicating that the amount of CH<sub>3</sub> groups were changed insignificantly. This is agreeable with the changes in MFI. It was assumed that both chain scission and crosslink were occurred but in comparable amount.

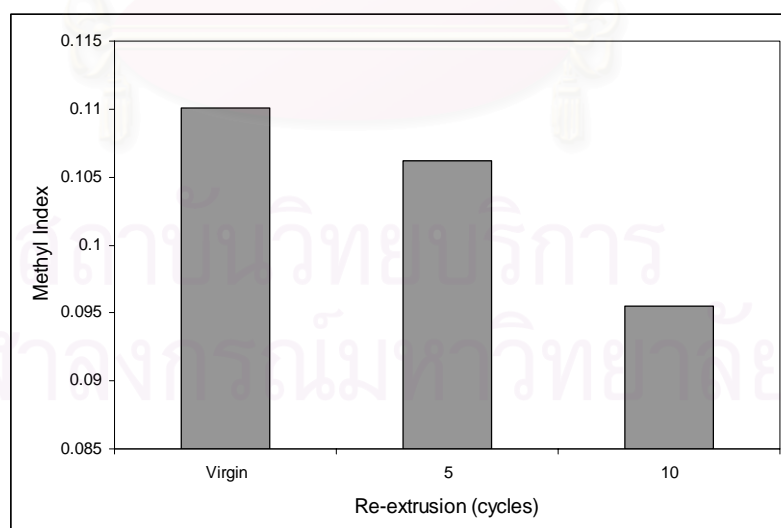


Figure 4.30 Methyl indices of re-extruded LDPE

#### 4.3.2 Tensile Properties

Generally, plastics loss their mechanical strength when they are subjected to heat and stress during the extrusion process.

Figure 4.31 shows the tensile strength of extruded LDPE passing through different re-extrusion cycles. Evidently, the tensile strength of re-extruded LDPE was insignificantly increased as the number of re-extrusion increased. However, we assumed that cross-linking also occurred but in less degree than that in HDPE. The same trend for the elongation at break was also found as shown in Figure 4.32.

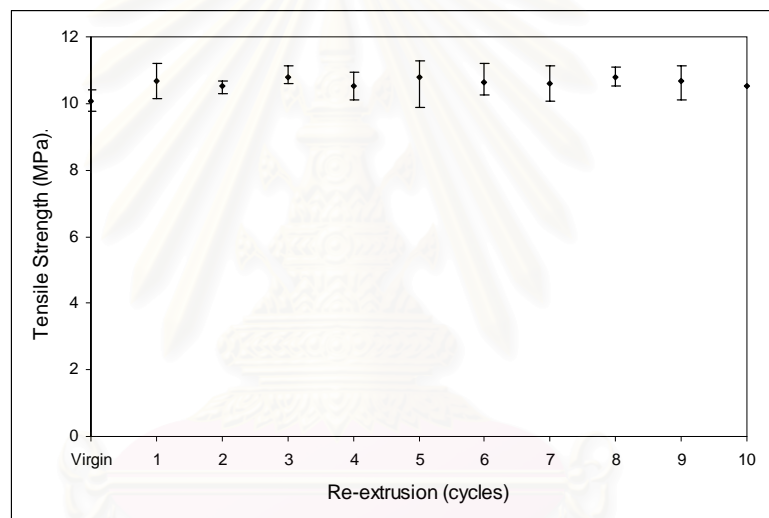


Figure 4.31 The tensile strength of re-extruded LDPE

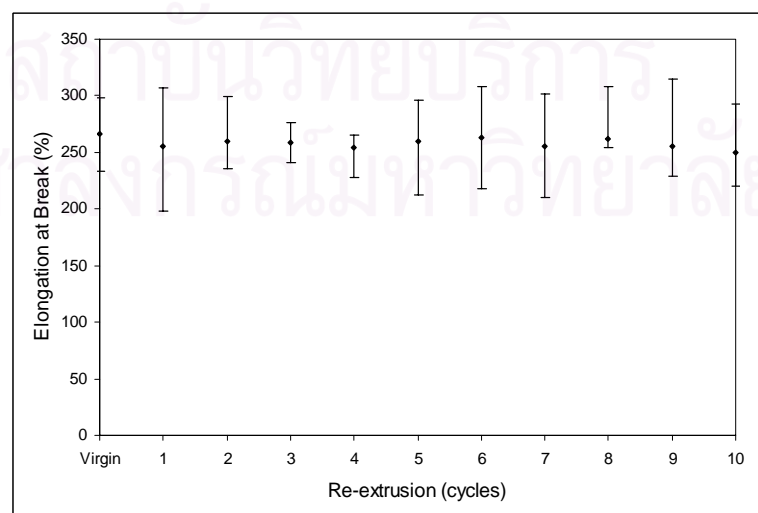


Figure 4.32 Elongation at break of re-extruded LDPE

Figure 4.33 shows the modulus of re-extruded LDPE that related to the molecular weight. The increasing of modulus was in the same trend as in tensile strength. This may arise from cross-linking occurred between molecular chains.

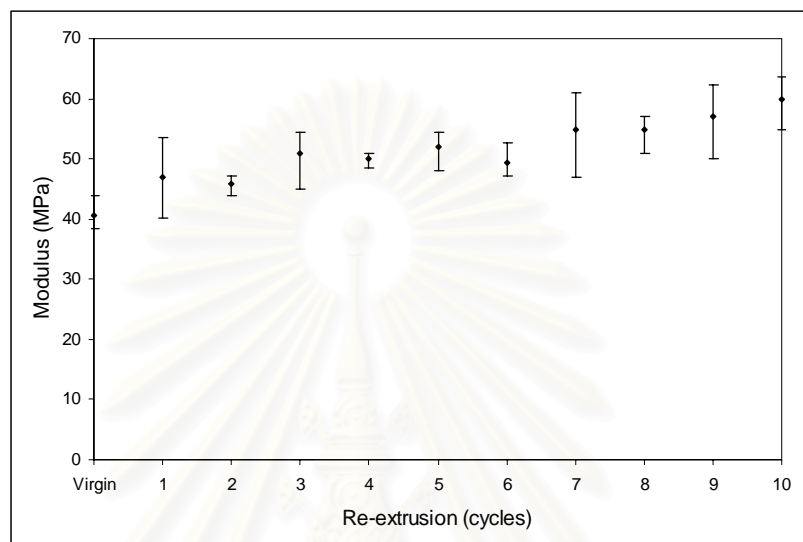


Figure 4.33 Tensile modulus of re-extruded LDPE

#### 4.3.3 Yellowing Phenomena

Figure 4.34 shows the value of yellowness. The yellowness is associated to the quantities of vinyl groups that occur during thermal degradation. The FT-IR analysis, as shown in Figure 4.35, pointed out that there were changes in the amount of vinyl groups when plastics were undergone the re-extruded. It was expected that the vinyl index should be increased. However it was pointed out in Figure 4.35 that the vinyl index was decreased. This was probably due to the fact that the amount of  $\text{CH}_2$  deformation was increased in the much larger extent than the increasing of the amount of vinyl group, resulting in the decreasing of vinyl index. The increase in  $\text{CH}_2$  groups was previously shown in Figure 4.30.

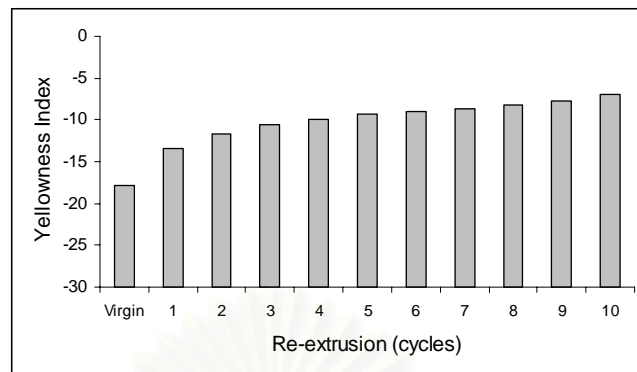


Figure 4.34 Yellowness of re-extruded LDPE

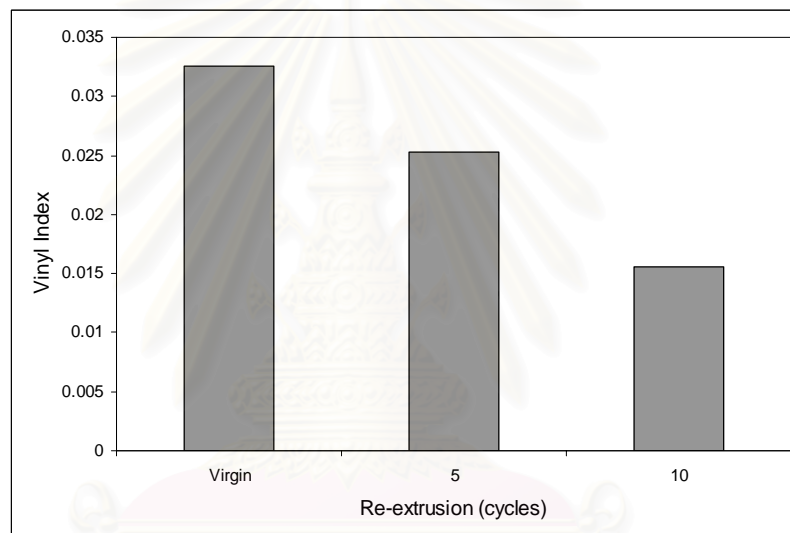


Figure 4.35 Vinyl indices of re-extruded LDPE

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## Chapter 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Molecular Structure Changes

Upon reprocessing, the molecular structures of plastics were changed. In this research, we used MFI to indicate such changes in plastics that varies from the processing as shown. In the case of extruded PP, the MFI was found to be increased assuming that chain-scission were dominant reaction as comparing to intermolecular cross-linking. The result was similar to injected PP. As for HDPE, The MFI of extruded HDPE and injected HDPE were decreased because HDPE chain cans crosslink with others. The MFI of extruded LDPE was constant.

It was found that tensile properties of re-processed plastics were changed upon simulated recycling. This was related to the changes in molecular structures as described earlier. For extruded PP, the tensile strength was constant but modulus was reduced as the number of re-processing cycles increased because of chain-scission which occurred during processing. Percentage strain at break, in the couple earlier cycles, was constant. In the case of injected PP, The tensile strength and percentage strain were constant, but modulus was reduced as the number of re-injection cycles increased because of chain-scission.

In the case of extruded HDPE, The tensile strength and modulus were increased. The percentage strain was decreased. For injected HDPE, the tensile strength was constant but modulus was increased in the earlier process, but in the 7<sup>th</sup> to 10<sup>th</sup> cycle modulus was decreased rapidly that resulting from intermolecular cross-linking. Later on, the percentage strain was slightly increased as the cross-linking polymer more than the chain scission. For extruded LDPE, The tensile strength was constant or slowly increases and modulus was increased resulting from intermolecular cross-linking



## 5.2 Yellowing Phenomena

Yellowing phenomena can be observed as plastics subjected to either extrusion or injection process. For PP, the rate of changes in yellowness index is higher in the case of injection process. As for HDPE, the rate of changes in yellowness index is higher in the case of extrusion process. The increase in yellowness index of HDPE was the most significant follows by LDPE and PP. This was the effects of bulky groups in polypropylene chains that prohibited the formation of chromophoric groups.

## 5.3 FT-IR Analysis

The changes of molecular structures during either extrusion or injection process were confirmed by FTIR techniques. From FTIR analysis, the ratio between absorbance at  $1370\text{-}1390\text{ cm}^{-1}$  indicating  $\text{-CH}_3$  symmetrical deformation and at  $1430\text{-}1470\text{ cm}^{-1}$  indicating  $\text{-CH}_2\text{-}$  and  $\text{-CH}_3$  deformation was calculated. This ratio is called the methyl index. In the case of PP, the methyl index has increased because plastics were passed the heating. We assumed that chain-scission occurred more than cross-linking. In the case of LDPE, the methyl index has decreased because LDPE contains many more branches that can crosslink, when it undergone the heating. Finally, HDPE has the decreasing, at the 5<sup>th</sup> cycle; in the methyl index implied that the molecular chains contain less methyl groups. Thus, cross-linking is assumed to be dominating reaction. At the 10<sup>th</sup> cycle, the methyl index indicated that either methyl groups were reduced or  $\text{-CH}_2\text{-}$  groups were increased. It can be implied that molecular chains were shorter due to chain scission.

## 5.4 Recommendations

Use of recycled plastics is possible as the mechanical properties are changed slightly. However, the altered MFI must be taken into account as it is very important to the processing technique. Changes in molecular weight can be seen more obviously. Thus, mixing recycled plastics with virgin plastics might worsen the properties of the blend products as molecular weight distribution is broaden.

## REFERENCES

- Ambrose, C. A., Hooper, R., Potter, A.,K., and Singh, M.M. Diversion from landfill: quality products from valuable plastics. Resources, Conservation and Recycling **36** (2002): 309-318.
- Association of Plastics Manufacturers in Europe. Consumption Data by Plastics Type [Online]. Available from: <http://www.apme.org> [2003, April 4]
- Bernado C.A., Cunha A.M. and Oliverira M.J. The Recycling of Thermoplastics: Prediction of the Properties of Mixtures of Virgin and Reprocessed Polyolefins Polymer Engineering and Science **36**(4), 1996.
- Berns, R.S., Principles of color technology, New York: John Wiley & Sons, 2000.
- Bodizar, A., Jansson, A., Gevert, T. and Moller, G. Simulated recycling of post-consumer high density polyethylene material. Journal of Polymer Degradation and Stability **68** (2000) 317-319.
- Brydson J. A., Plastics Materials. 4<sup>th</sup> ed. London : Butterworths Scientific, 1982.
- Ehrig, R.J., ed. Plastics Recycling: Products and Processes. New York: Oxford University Press, 1989.
- George, G. A., Celina, M., Vassallo, A. M., and Cole-Clarke, P. A. Real time analysis of thermal oxidation of polyolefins by FT-IR emission. Polymer Degradation and Stability **48** (1995): 199-210.
- Immediate Technology Development Group. Recycling Plastics [Online]. Available from: <http://www.itdg.org/> [2004, March 16]
- Incarnato, L., Scarfato, P., and Acierno, D. Rheological and Mechanical Properties of Recycled Polypropylene. Polymer Engineering and Science **39**(4): 749-755, 1999.

- Industrial Designers Society of America Materials and Processes Section. Plastic: Injection Molding [online]. Available from: <http://www.idsa-mp.org> [2003, September 27]
- Kelen, T. Polymer Degradation. New York: Van Nostrand Reinhold, 1983.
- Moton-Jones, D.H. Polymer Processing. New York: Chapman and Hall, 1989.
- Miller, P., Sbarski, I., Kosior, E., Masood, S., and Iovenitti, P. Correlation of Rheological and Mechanical Properties for Blends of Recycled HDPE and Virgin Polyolefins. Journal of Applied Polymer Science 82(14): 3505-3512, 2001.
- Santos, A. S. F., Agnelli, J.A.M., Trevisan, D.W., and Marich, S. Degradation and stabilization of polyolefins from municipal plastic waste during multiple extrusions under different reprocessing conditions. Polymer degradation and stability 77 (2002): 441-447.
- Schnabel, W. Polymer Degradation: Principles and Practical Applications. Munich: Hanser, 1981.
- Sperling, L.H. Introduction to Physical Polymer Science. 2<sup>nd</sup> ed. New York: John Wiley & Sons, 1993.
- Stevens, M.P. Polymer Chemistry: An Introduction. New York: Oxford University Press, 1999.
- Suarez, J. C. M., Monteiro, E.E.D.C., and Mano, E.B. Study of the effect of gamma irradiation on polyolefins low-density polyethylene. Polymer Degradation and Stability 75 (2002):143-151.
- Yamaradi, N., Jakubowicz, I., and Gevert, T. Effects of repeated extrusion on the properties and durability of rigid PVC scrap. Polymer Degradation and Stability 73(2001):93-99.

Appendix



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## APPENDIX A

### MELT FLOW INDEX RESULTS

#### A.1 Extrusion

##### A.1.1 Polypropylene

cycle	MFI (g/10min)	SD
Virgin	4.526	0.027019
1	4.658	0.05671
2	4.7	0.109545
3	6.1	0.147648
4	6.808	0.259461
5	6.94	0.427785
6	8.716	0.437299
7	9.106	0.249159
8	10.21	0.044721
9	12.208	0.041473
10	14.174	0.026077

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## A.2 Low Density Polyethylene

cycle	MFI (g/10min)	SD
Virgin	4.568	0.008367
1	4.628	0.016432
2	4.58	0.021213
3	4.622	0.019235
4	4.672	0.047645
5	4.714	0.037815
6	4.73	0.018708
7	4.75	0.012247
8	4.756	0.018166
9	4.764	0.011402
10	4.758	0.008367

### A.2.1 High Density Polyethylene

cycle	MFI (g/10min)	SD
Virgin	0.81834	0.003235
1	0.73106	0.005154
2	0.57	0.015811
3	0.466	0.011402
4	0.408	0.008367
5	0.362	0.008367
6	0.30878	0.004479
7	0.25542	0.00137
8	0.23728	0.001197
9	0.26338	0.001757
10	0.2847	0.002683

### A.3 Injection

#### A.3.1 Polypropylene

cycle	MFI (g/10min)	SD
Virgin	12.08	0.178885
1	12.8	0.282843
2	16.32	0.334664
3	17.936	0.543029
4	18.948	0.597595
5	23.688	0.237739
6	26.192	1.194119
7	28.8	1.235476
8	36.615	0.890449
9	43.992	0.639781
10	47.04	0.916842

#### A.3.2 High Density Polyethylene

cycle	MFI (g/10min)	SD
Virgin	7.68	0.127279
1	7.092	0.130077
2	6.232	0.29853
3	5.864	0.19718
4	5.688	0.117983
5	5.48	0.15748
6	5.016	0.092087
7	5.024	0.115239
8	4.8	0.056569
9	4.258	0.161307
10	4.256	0.045607

## APPENDIX B

## TENSILE TEST RESULTS

## B.1 Extrusion

B.1.1 Polypropylene

cycle	Tensile Strength		Elongation at Break		Modulus	
	MPa	SD	%	SD	MPa	SD
Virgin	36.15	1.29	73.50	7.81	184.87	13.06
1	36.14	0.93	69.69	18.78	184.86	13.04
2	36.45	0.75	66.03	11.49	176.97	20.50
3	36.37	0.82	69.69	7.35	168.00	21.75
4	35.85	0.87	65.32	3.94	166.30	22.72
5	36.26	0.75	63.55	10.36	165.01	15.37
6	35.24	1.02	66.82	10.55	165.49	4.91
7	35.34	1.17	67.06	10.52	161.32	6.63
8	35.29	1.04	73.14	7.37	158.06	19.24
9	35.76	0.75	71.44	16.75	143.82	34.54

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B.1.2 Low Density Polyethylene

cycle	Tensile Strength		Elongation at Break		Modulus	
	MPa	SD	%	SD	MPa	SD
Virgin	10.07	0.32	266.52	27.80	40.68	2.11
1	10.67	0.42	255.38	38.49	46.87	53.46
2	10.51	0.16	260.02	26.06	45.84	12.40
3	10.80	0.23	258.14	12.99	50.87	33.81
4	10.54	0.32	238.66	9.97	50.06	11.22
5	10.79	0.52	259.45	44.87	52.00	25.68
6	10.62	0.33	262.53	31.87	49.38	20.07
7	10.59	0.42	254.80	37.87	54.90	47.76
8	10.80	0.22	270.52	22.19	54.80	25.42
9	10.69	0.34	255.33	30.65	57.10	54.14
10	10.51	0.23	249.63	25.65	59.88	3.83

B.1.3 High Density Polyethylene

cycle	Tensile Strength		Elongation at Break		Modulus	
	MPa	SD	%	SD	MPa	SD
Virgin	23.61	1.69	87.50	12.77	123.68	6.23
1	22.47	5.22	85.98	18.01	132.76	18.07
2	23.99	3.00	82.83	8.21	133.00	7.00
3	24.57	0.74	80.79	13.23	149.55	1.03
4	24.96	0.74	78.52	13.23	150.87	10.28
5	24.70	0.80	80.16	10.39	151.73	2.73
6	25.21	0.66	73.10	4.37	152.28	3.99
7	25.65	0.39	73.49	16.35	152.85	6.01
8	25.19	0.69	75.89	9.03	152.83	2.14
9	25.41	0.82	70.40	3.37	153.17	3.25
10	25.31	0.87	80.49	7.13	154.20	8.07

## B.2 Injection

### B.2.1 Polypropylene

cycle	Tensile Strength		Elongation at Break		Modulus	
	MPa	SD	%	SD	MPa	SD
Virgin	42.94	0.34	23.28	0.40	287.67	9.57
1	43.18	0.24	22.89	0.80	292.30	8.47
2	43.44	0.24	23.56	0.29	284.03	7.01
3	42.99	0.16	23.09	0.37	288.53	5.43
4	43.11	0.39	22.86	1.12	282.91	15.66
5	43.87	0.14	23.03	0.73	271.71	12.02
6	44.06	0.05	22.63	0.97	266.83	12.77
7	43.65	0.15	22.66	0.55	273.14	15.81
8	43.39	0.05	23.07	0.31	247.80	13.77
9	43.47	0.36	22.38	0.37	248.17	13.47
10	42.93	0.12	21.73	0.62	196.50	25.65

B.2.2 High Density Polyethylene

cycle	Tensile Strength		Elongation at Break		Modulus	
	MPa	SD	%	SD	MPa	SD
Virgin	23.35	0.24	30.22	1.12	83.91	12.92
1	22.29	0.41	27.04	1.33	130.99	14.46
2	22.99	0.69	27.03	0.57	138.15	9.22
3	22.58	0.69	26.94	1.01	134.06	9.47
4	22.64	0.42	26.88	1.14	136.78	9.50
5	23.28	0.48	29.12	1.19	142.38	14.33
6	23.14	0.50	31.18	0.90	132.12	9.36
7	23.61	0.29	29.75	1.15	91.29	5.52
8	23.28	0.47	29.50	0.97	96.31	7.74
9	23.32	0.25	29.31	0.97	88.38	9.45
10	23.33	0.49	28.81	1.14	101.48	9.94

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## APPENDIX C

## YELLOWNESS INDEX RESULTS

## C.1 Extrusion

C.1.1 Polypropylene

cycle	YI	SD
Virgin	-5.16	0.00
1	-4.13	0.31
2	-3.64	0.31
3	-3.21	0.31
4	-2.84	0.01
5	-1.90	0.01
6	-1.78	0.04
7	-1.05	0.08
8	-0.54	0.04
9	0.34	0.06
10	2.42	0.16

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C.1.2 Low Density Polyethylene

cycle	YI	SD
Virgin	-17.84	0.00
1	-13.83	0.49
2	-12.19	0.66
3	-11.18	0.84
4	-10.71	1.03
5	-10.06	1.04
6	-9.54	0.71
7	-9.22	0.67
8	-8.73	0.69
9	-8.32	0.83
10	-7.28	0.52

C.1.3 High Density Polyethylene

cycle	YI	SD
Virgin	-25.23	0.00
1	-21.70	0.01
2	-19.32	0.51
3	-16.89	1.85
4	-13.48	2.52
5	-11.61	0.58
6	-9.81	1.97
7	-5.75	1.00
8	-0.31	0.42
9	4.61	1.29
10	6.58	0.22

## C.2 Injection

### C.2.1 Polypropylene

cycle	YI	SD
Virgin	-22.11	0.25
1	-17.55	0.17
2	-16.02	0.33
3	-10.79	0.64
4	-8.64	0.03
5	-6.65	0.07
6	-5.66	0.06
7	-4.74	0.93
8	-3.26	0.14
9	-2.72	0.09
10	-2.10	0.01

### C.2.2 High Density Polyethylene

cycle	YI	SD
Virgin	-8.95	0.13
0	-7.61	0.20
1	-6.16	0.21
2	-4.54	0.17
3	-3.38	0.43
4	-1.86	0.13
5	-0.68	0.20
6	1.08	0.06
7	1.64	0.11
8	3.09	0.23
9	3.76	0.09
10	-8.95	0.13

## APPENDIX D

## FOURIER TRANSFORM INFRARED SPECTROSCOPY

## D.1 Extrusion

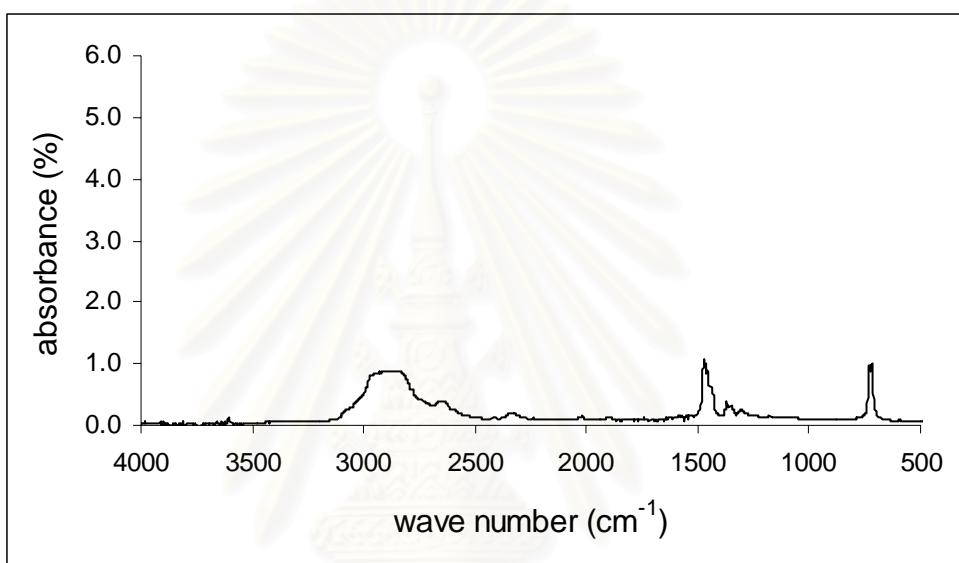
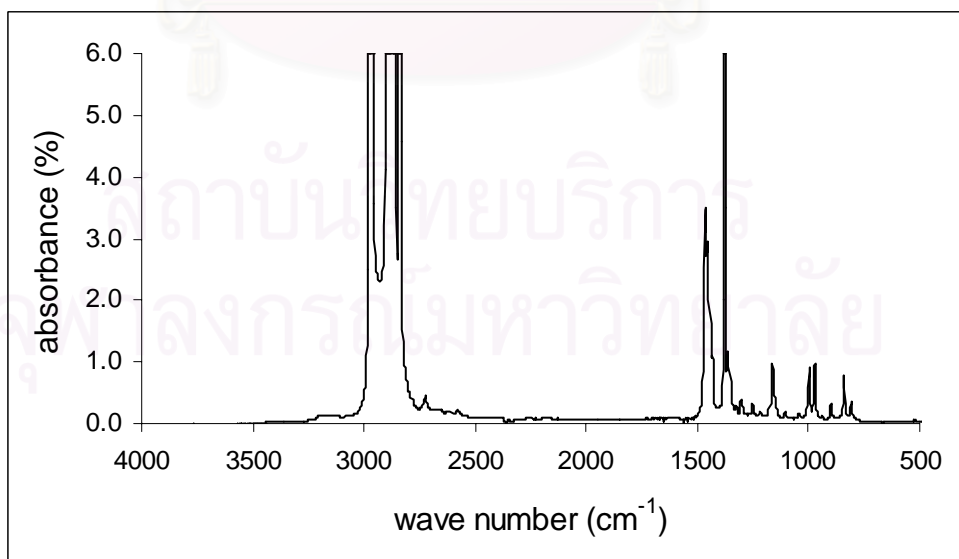
D.1.1 Polypropylene

Figure D.1 FT-IR spectrum of virgin sample

Figure D.2 FT-IR spectrum of 5<sup>th</sup> cycle re-extruded sample

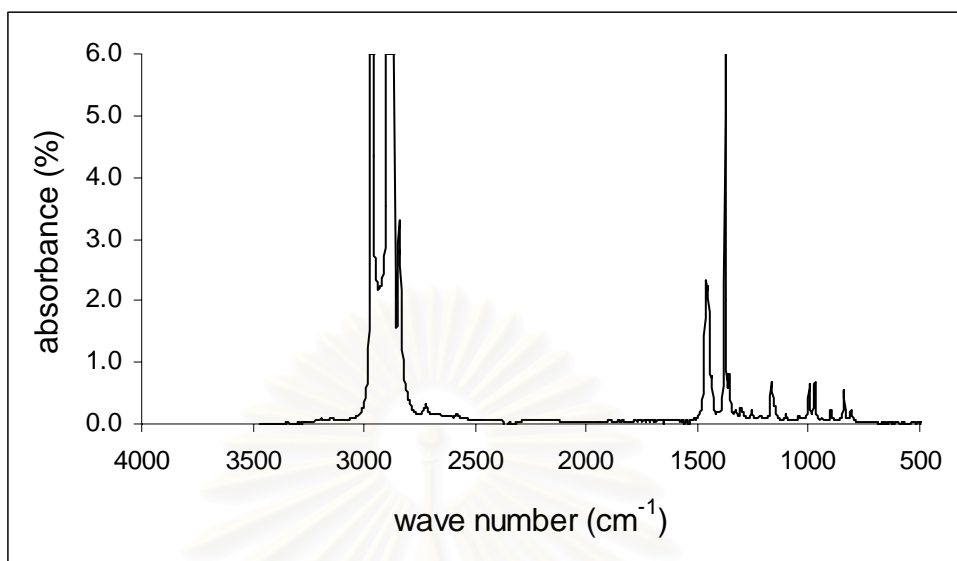


Figure D.3 FT-IR spectrum of 10<sup>th</sup> cycle re-extruded sample

#### D.1.2 Low density polyethylene

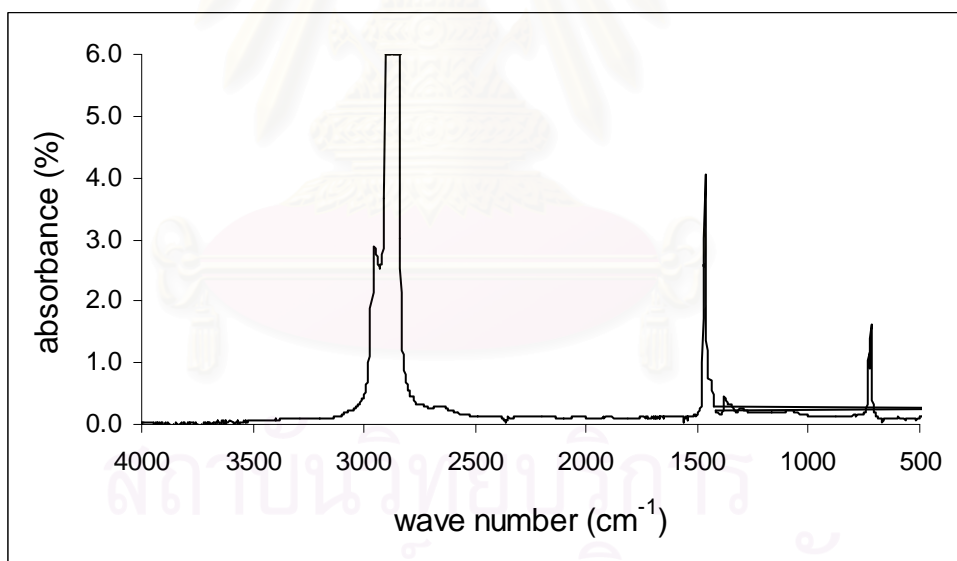
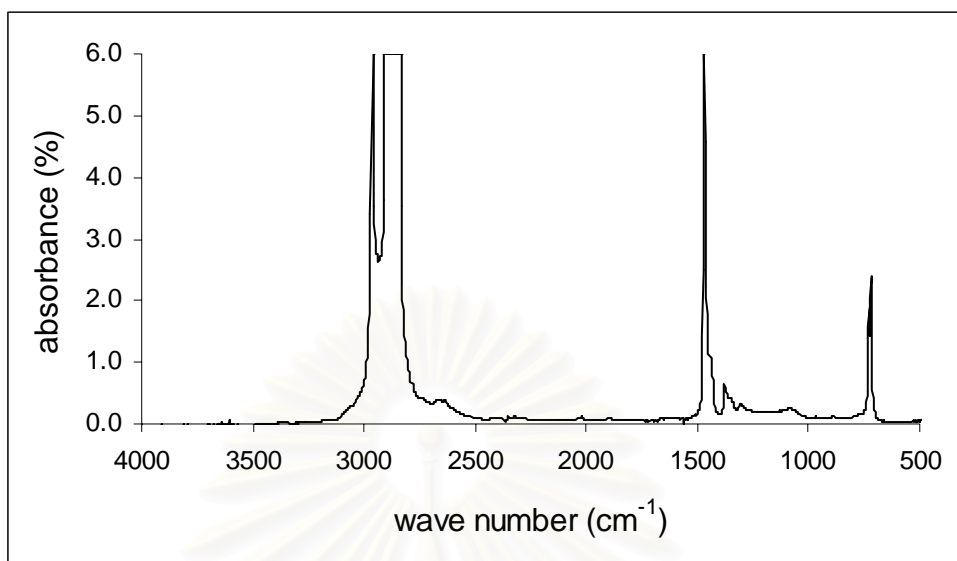
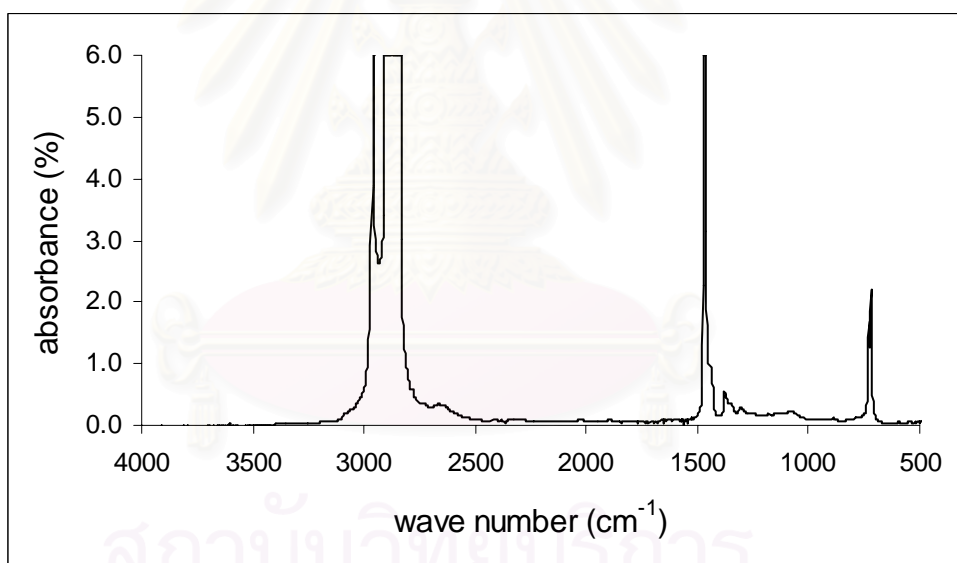


Figure D.4 FT-IR spectrum of virgin sample



Figure D.5 FT-IR spectrum of 5<sup>th</sup> cycle re-extruded sampleFigure D.6 FT-IR spectrum of 10<sup>th</sup> cycle re-extruded sample

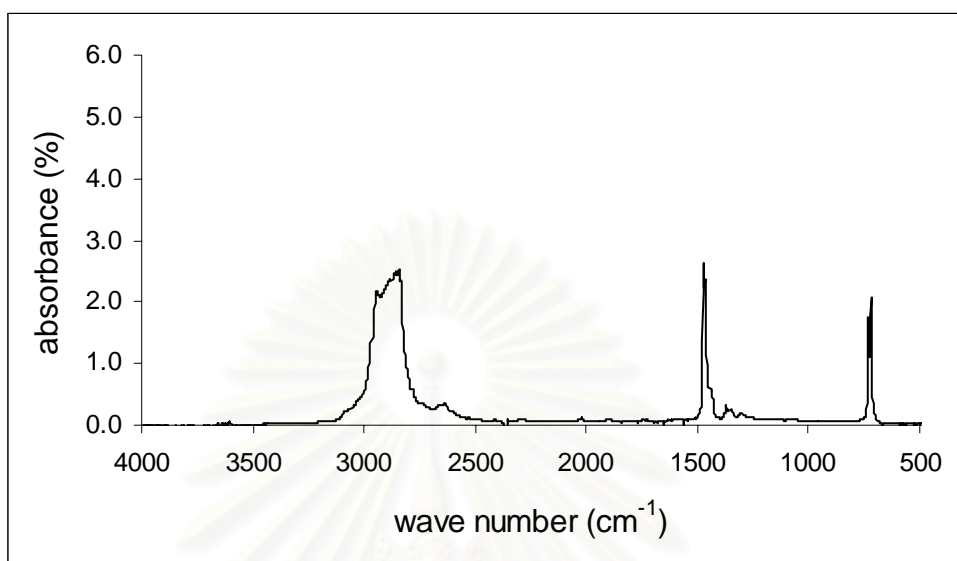
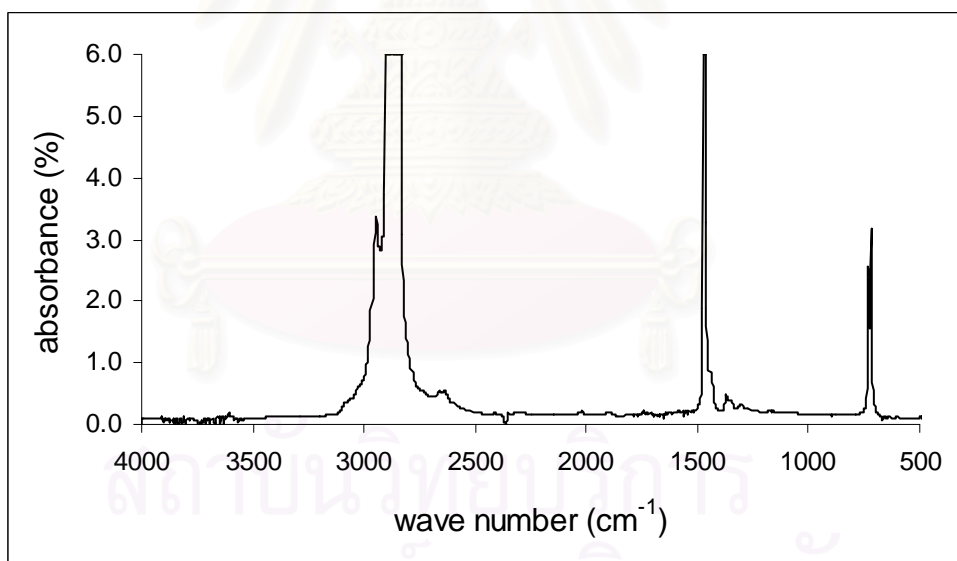
D.1.3 High Density Polyethylene

Figure D.7 FT-IR spectrum of virgin sample

Figure D.8 FT-IR spectrum of 5<sup>th</sup> cycle re-extruded sample

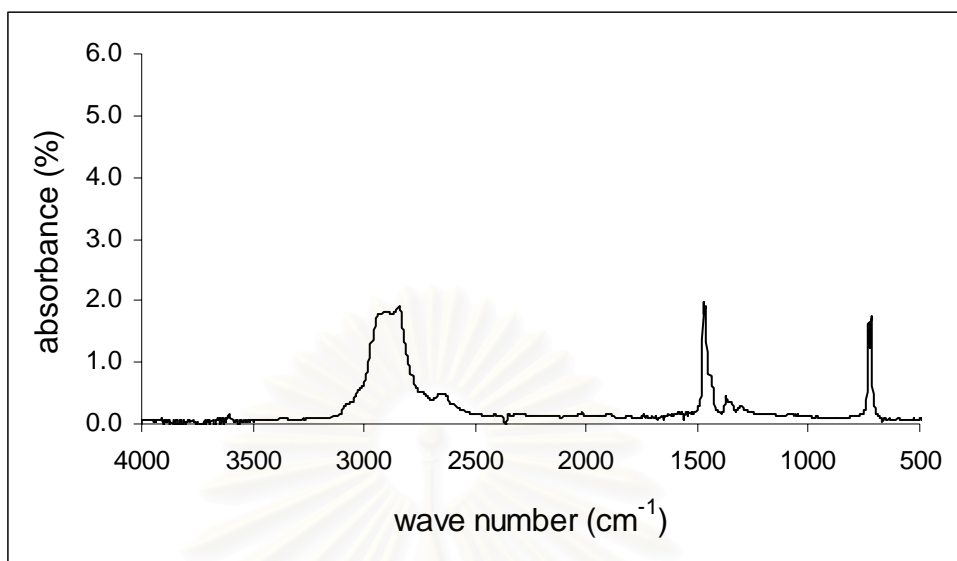


Figure D.9 FT-IR spectrum of 10<sup>th</sup> cycle re-extruded sample

## D.2 Injection

### D.2.1 Polypropylene

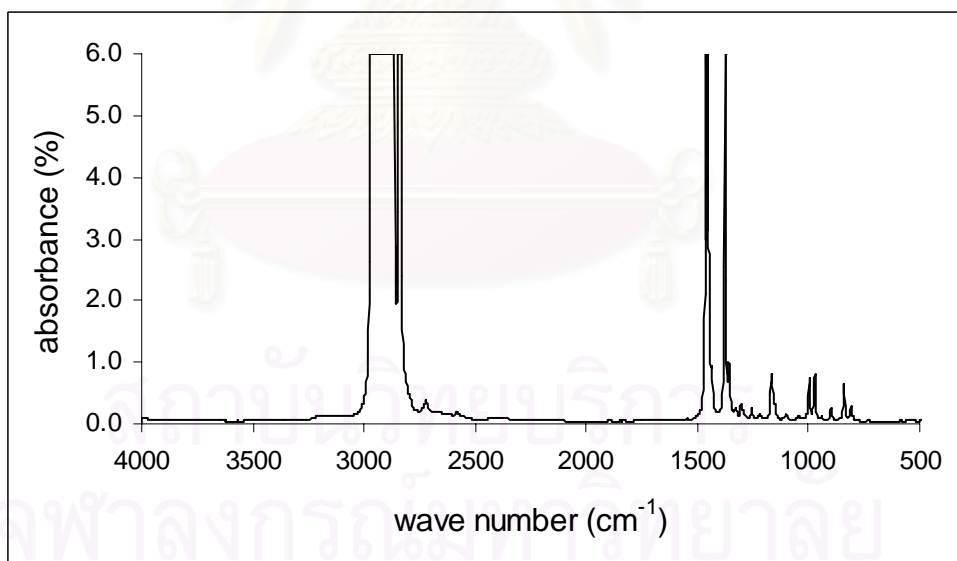
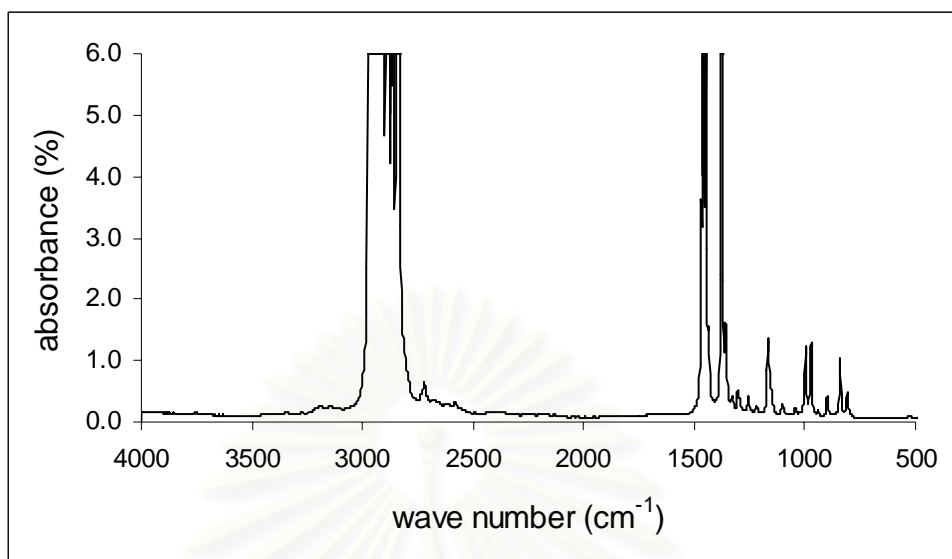
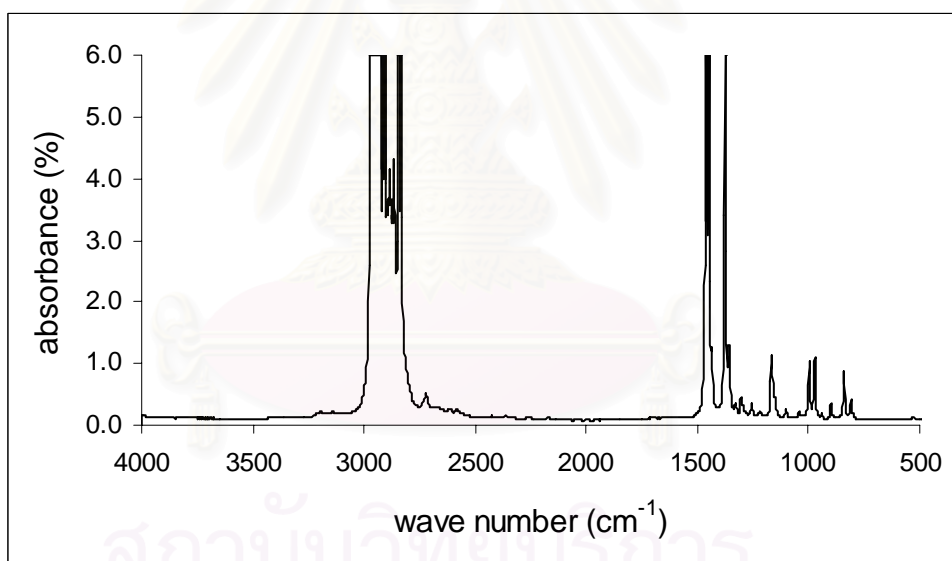


Figure D.10 FT-IR spectrum of virgin sample

Figure D.11 FT-IR spectrum of 5<sup>th</sup> cycle re-injected sampleFigure D.12 FT-IR spectrum of 10<sup>th</sup> cycle re-injected sample

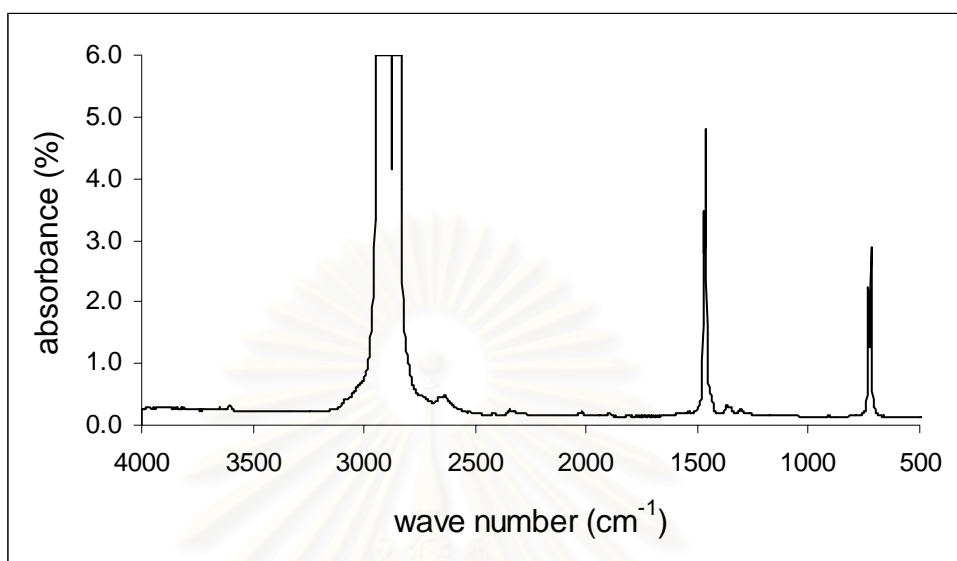
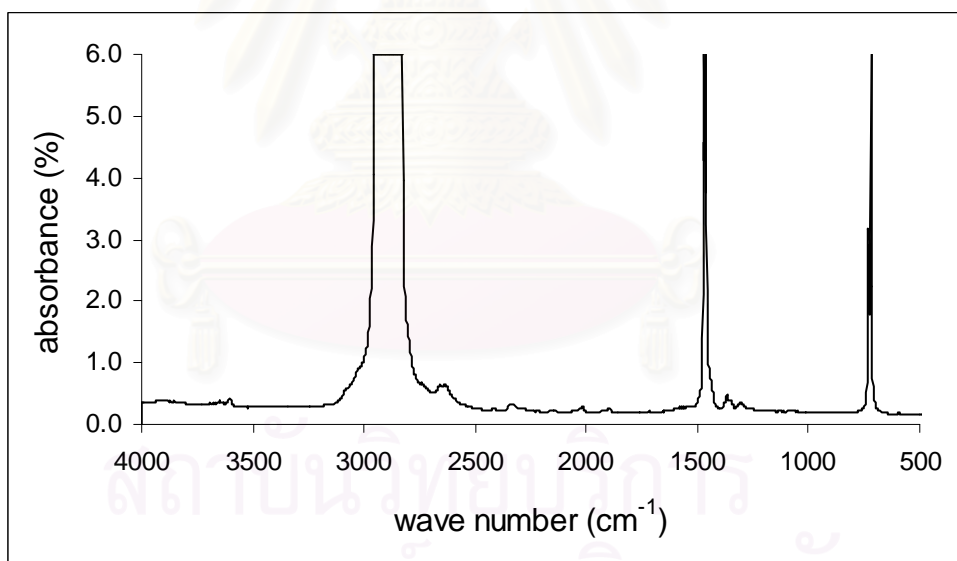
D.2.2 High Density Polyethylene

Figure D.13 FT-IR spectrum of virgin sample

Figure D.14 FT-IR spectrum of 5<sup>th</sup> cycle re-injected sample

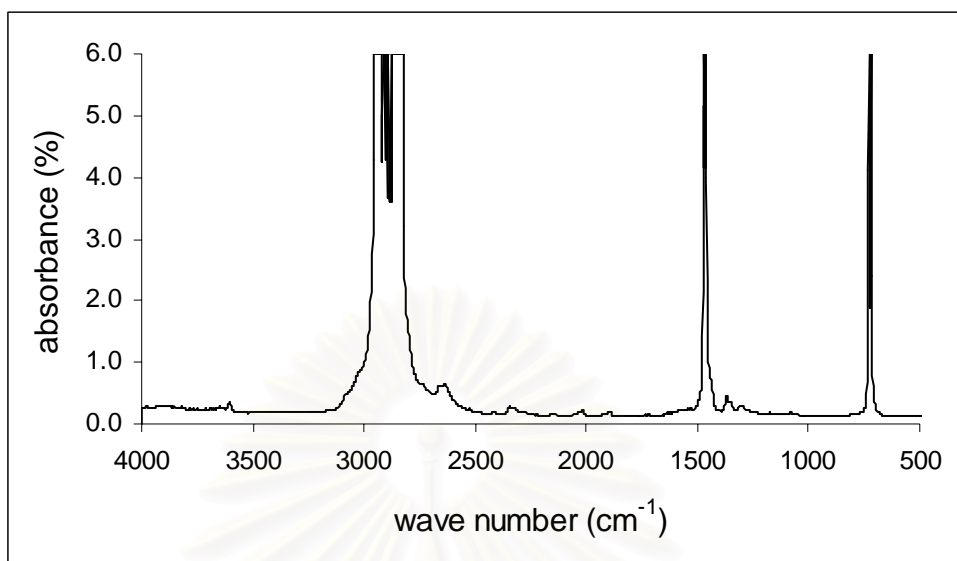


Figure D.15 FT-IR spectrum of 10<sup>th</sup> cycle re-injected sample

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## BIOGRAPHY

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